Proceedings

THE SIXTH SYMPOSIUM
ON THE
ART OF GLASSBLOWING

1961

THE

AMERICAN SCIENTIFIC GLASSBLOWERS SOCIETY

Proceedings
THE SIXTH SYMPOSIUM
ON THE
ART OF GLASSBLOWING

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FOREWORD

Time, or the passing of time, reminds us not only of the past but the future, and man has continually strived to contribute to the future something better than he experienced. Perhaps he was thinking of the welfare of his children or his grandchildren as this is probably one of the motivating forces that lead people to explore and find new sources of raw material, develop new techniques and new tools.

New Materials and new methods + new tools + effort = progress.

Today much of the exploration and development is done in the research laboratory and much of the advance in our general welfare is made possible by the products of the electronics industry, many of which contain glass and therefore has a close affinity to the glass man.

For the above reason it was decided that the Formal Sessions of this Sixth Symposium on the "Art of Scientific Glassblowing" should highlight electron tube research.

Therefore, many of the technical papers contained in these "Proceedings" are directly or indirectly associated with the electronics industry, and I take this opportunity to officially thank all of the authors and their sponsors on behalf of The American Scientific Glassblowers Society for their contribution to the success of this Sixth Symposium.

Another innovation which materially contributed to the success of this Symposium were the "Workshop Discussion Sessions" which were so arranged to give the widest possible scope of general subject matter on an informal basis for maximum benefit of all phases of glassblowing on a practical level. These discussion sessions have been tape recorded and are available upon compliance with certain provisions. The recordings along with these "Proceedings" make the fruits of this Sixth Symposium available to those not able to attend in person.

The success of this Sixth Symposium and Second Exhibit was largely due to the untiring efforts of the Symposium Committee, and our Society is fortunate to have members of such outstanding calibre and ability willing to serve.

J. ALLEN ALEXANDER,
President and Founder

CONTENTS

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KEYNOTE ADDRESS

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Mr. Chairman, Members of the Society and Guests:

When your Chairman invited me to talk to you this morning, I was at a loss for quite some time how I could justify in a straightforward manner my appearance on this platform. True enough, I have done some glassblowing, I have built hundreds of tubes with my own hands, I have even written about glass and glass-forming techniques, and taught others how to master this art; all this might not be very convincing to you who earn a living as members of the glassblowers' fraternity. Then I remembered that I was carrying around with me all the time a visible sign of my exposure to glassblowing and I want to show it to you. You see, I cannot bend my right thumb as much as my left one because I cut the tendons of my right thumb on a piece of glass when I was building a vacuum system during my college days in Germany. So, I am a real glassblower, and from the Old Country at that!

In those days we were not so fortunate as having a trained glassblower at our laboratory, but a student engaged in experimental work had to learn the rudiments of glassblowing so as to be able to build his own vacuum system and make the necessary repairs. Only when more complicated apparatus was needed could we engage the services of a professional man who ran a business nearby. Some of my friends achieved some advanced degree of skill and applied this very effectively to the making of Christmas tree decorations. I understand that this sort of activity is still a popular pastime even among instrument makers, and the purchasing agent at their institution must often wonder why colored glass is required for the production of scientific apparatus.

When scanning the titles on the program for this Symposium and at the same time glancing back over the 30 years which have passed since I left college, one cannot help but be impressed by the great strides which have been made in applying glass to the ever-growing needs of science and industry. Many new techniques have been developed for the forming and joining of glass, new glass compositions have been evolved to meet the very-low- and very-high-temperature applications, and even the transformation from the glassy to the crystalline state has been achieved by the introduction of Glass Ceramics* or Pyroceram,* or Cervit.†

Commercial glass has a very low nucleation rate so that it can be cooled from the molten state without devitrification. By adding suitable nucleating agents to the glass melt, the rate of nucleation can be substantially increased in selected ranges of supercooling. The bulk of the glass can then be transformed into a fine-grained ceramic on heating while maintaining the physical shape it was given on molding in the glassy state.

On studying this quite intricate mechanism of transformation and the details on which it depends, glass technologists have learned a good deal about

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*Trade name, Corning Glass Work, Corning, New York.
†Trade name, Kimble Glass Co., Toledo, Ohio

glass itself. Research on the fundamental nature of glass has been severely neglected at universities in the United States (E. U. Condon, 1955), and it is to be hoped that this area will receive new impetus from technological advances made in industrial laboratories. The development of high-temperature glasses with an annealing point close to 900°C. is an example about which we will hear more in a paper scheduled on this program tomorrow.

It cannot be the purpose of this introductory address to review in any detail the content of the papers which you are to hear during the Symposium. The subjects cover a wide range. As a guest speaker, I may be permitted to compliment your program chairman on the high level which he has established for this Conference. What is in order, I believe, is to raise the question: What impact do all these new techniques and the increasing complexity of our technology in general have on the structure and purpose of a technical society and particularly on the objectives of The American Scientific Glassblowers Society? This question has been discussed at some length by Dr. C. H. Loviz who is Technical Director of Batelle Memorial Institute. I should like to quote a few statements from his paper entitled: "The Role of Technical Societies."[1]

> "The primary task of technical societies has been and will continue to be the promotion of education.
>
> "A technical society must remain alert to a changing technology. Remaining static for a period as short as five years can do irreparable damage to an organization. Leaders of a technical society must, therefore, remain aware that a new scientific discovery may suddenly lessen—or even eliminate —the need for the society.
>
> "Methods must be found for adjusting the structure of societies to take account of the specialized and newly acquired interests of their members."

Let me now speculate for a moment on the implications which these statements may have on your Society in particular. I do this as a complete outsider, without prompting from any of your officers, even without any knowledge of your mode of operation, but based on the belief that you are a fairly recent association of highly skilled craftsmen dedicated to the working of glass in all its many applications. A very large body of experience and know-how is thus represented in this audience. In days gone by, it used to be the practice among glassblowers to guard such know-how jealously and do everything possible to prevent its dissemination. As a young man, I nearly lost my job at one time when I passed on to a university laboratory the taper dimensions for a tubular Houskeeper* seal which was used in the production of power tubes at the plant where I was employed. This was a sufficiently serious offense to warrant the president of the company giving me a gentle dressing down. Fortunately, this attitude is rapidly becoming a thing of the past. This competitive position of a company is best maintained not by guarding old tricks but by continuously striving for new advances and maintaining leadership in its particular field of endeavor. There is justification for guarding a new process against premature disclosure during a short lead-time until legal protection has been established, but then it should be made available to the profession at large.

Like every other association, your Society has a very considerable responsibility in ensuring the most effective education of its members and making available to them with a minimum of delay new information which has been published

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*Mr. Houskeeper was not a housekeeper, he spells his name without the "e" after the "s."

in the literature or evolved from work of its members. This is an enormous task, and I wonder whether it is being met effectively. I am pleased to note that several papers on the program are devoted to this topic of education and training.

It is unfortunately true that adequate facilities for the schooling of young people who wish to become glassblowers, or glass technicians in the broader sense, are lacking in this country. Most of you have probably stumbled into this trade by accident and gained your experience on the job. This is not the best approach to a profession. A full appreciation of the problems which face the glass technician from day to day requires a degree of sophistication which can hardly be acquired without a much more thorough preparation. At the same time, challenging opportunities are open to a practically inclined young person with native curiosity if he should find himself working in a scientific laboratory where the tools for tomorrow's breakthrough are shaped. These career possibilities should be brought to the attention of high school students and their counsellors. Managers of laboratories in industry, government, and research institutions should be persuaded to provide regular on-the-job training programs for these young people, and the scientists with whom they work should take an active interest in their further development. Your Society could perform a valuable service by promoting this approach in an organized manner. I fully realize that all these programs cost money, but I see no reason why funds could not be raised for their execution from government and industry, if the plans are carefully prepared and carried forward with the cooperation of all interested parties. Your Society Journal could of course be an effective tool for the promotion of these objectives.

Let me now touch on another subject of great importance which has been discussed repeatedly in recent years and which is of great concern to many critical observers of our times. As a result of the trend toward ever greater specialization in all areas of endeavor there is great danger that the inner cohesion of our society—the human society—be lost. A great gulf exists between the scientists and the public at large. The public may admire the scientists' achievements but nevertheless view the egg-heads with suspicion and distrust. The man on the street does not understand the scientist's language and looks upon him as an outsider. Large surveys have been conducted in recent years to determine the image of scientists prevailing among high school students, college students, and faculty members. The results of these carefully conducted studies make it apparent that misunderstanding prevails not only between intellectuals and laymen but also at the college level between the men trained in the liberal arts and those devoted to the study of natural sciences, the scientists *per se*. Many people, especially young students, look upon the scientist as a highly intelligent person who is dedicated to the pursuit of his calling at the exclusion of any broader interests; he is believed to be unsociable, introverted, without friends, to have an unhappy homelife, and a wife who is not pretty. Some of the girls who were interviewed in the course of the survey, thought it inadvisable to double-date with a scientist and believed that he should not get married. He is assumed to be coldly intellectual in his professional area and emotional in his response to social and political appeals; he is not a cultured intellectual, not well-rounded, according to these views, and thus definitely set apart from the college professor in other disciplines. These misconceptions about the nature of scientists will often prevent high school students from choosing a career for which they are basically suited and, on the other hand, encourage those who fit this wrong image, to become frustrated scientists.[2]

I should like to suggest to members of this Society who have daily contact with scientists in their work to help dissipate these misconceptions whenever possible. I would further emphasize that you as craftsmen who often fashion the tools with which important scientific advances are made have an opportunity to explain to your neighbors and friends that science is not all fancy dreaming and theory, but that very practical problems must often be solved before such dreams can be realized. The development of the microscope depended on the skill of the lens grinder, the functioning of the iconoscope requires uniform glass targets thinner than a human hair which a glass blower must produce, and the viewing ports of space ships present challenges to the glass technologist which will be described during this Symposium.

Science is one of the very few areas where the people of the civilized world agree on the basic issues. Our lives will be fashioned to an ever-increasing extent by the advances of science. A broad public support of science is essential before these advances can come about with sufficient frequency to enable this country to stay in the race with our competitors in other lands. Anyone connected with science, be it on a theoretical or a practical plane, as you are, should thus help to broaden this much-needed understanding of the aims of science by the common man. You are more likely to succeed in carrying this message to your friends who are not scientists because they will understand it when you talk about something which you produce with your hands and at the same time convey to these doubting Thomases an inkling of the far-reaching projects to which scientists have dedicated themselves. We need both the skills of the hands and those of the mind to succeed. "We must have respect for both our plumbers and our philosophers or neither our pipes nor our theories will hold water."[3]

At this point, I am faced with a slight dilemma. When I have written a paper, I always ask my wife to read it and comment on its overall composition. Usually she picks up a few errors which have escaped my scrutiny. There was a loud protest at this junction however. She frankly admitted that the technical aspects of the following section were beyond her grasp, but claimed that there ought to be a transition, preferably a smooth one. Well, what I have just said is a warning to you that I am about to switch gears.

We have discussed, so far, the obligations of a technical society, some educational problems, and the possibility of dispersing some misconceptions about the nature of scientists. During the remainder of the time allotted to me, I should like to give some examples of theoretical problems related to glassblowing and talk about *The Art and Science of Materials Joining.* We will thus have to investigate the very broad question: What causes two materials to stick to each other? What conditions must be satisfied to establish a permanent bond? There are several different types of bonds; some of these are not at all well understood, but nevertheless widely used. Let us look at some examples.

You know how tightly two Johansson gauge blocks will adhere to each other when most of the air has been eliminated from the interface by sliding one of the blocks over the other. A force of 400 psi is required to separate them. You know how friction between certain materials is increased in vacuum. (There exists a critical temperature for the onset of normal adhesion of metals in vacuum which ranges from 30°C, for indium and lead, to 250°C for gold, and 620°C for platinum.)

When a gold washer is placed between two copper parts and the joint is heated to 450°C for about an hour while moderate pressure is applied, a vacuum-tight diffusion seal results at a temperature which is well below that at which the gold-copper eutectic is formed (889°C.). Interdiffusion occurs at the boundary of optically polished glass surfaces at elevated temperature and pressure, and this effect has been utilized for the production of vacuum-tight joints in electron tubes. The more conventional glass-to-metal seals rely on the diffusion of an oxide layer, produced on the metal, into the glass body. (Compression seals, on the other hand, can be made in a neutral atmosphere and do not rely on the oxide bond.)

Another class of bonds depends primarily upon chemical forces; most adhesives fall into this category. At a clean surface the force field differs from that prevailing within the bulk of the material because the spacial symmetry is disturbed, and free valencies exist which can be satisfied by compound formation. A free surface is thus chemically active and tends to extend itself by adsorbing materials which satisfy the original structure and force field of the base layer. This type of surface extension is known as epitaxial growth and has found recent application in the design of transistors. Continuation of the glass structure with other building units is responsible for the adhesion of magnesium fluoride and calcium fluoride when these substances are deposited from the vapor phase onto lenses and prisms as anti-reflection coatings. These fluorides have a structure which matches that of the constituent oxides of the glass, and the salts of the ions are soluble in the glass melt.

Extremely clean surfaces are required before these surface forces can contribute to the formation of a bond. Initially clean glass, when exposed to the atmosphere, will attract water molecules and become covered with a layer of OH molecules through hydrolization. This hydroxide layer is effectively removed only by a rinse in dilute hydrofluoric acid and not by the conventional chromic acid cleaning solution, as Todd and his coworkers have pointed out in their studies on the outgassing of glass. On the other hand, "these hydroxyl groups are responsible for the adhesion of many organic compounds, such as high polymers and animal glue, where reactive carboxyl and amino groups can interlink with the hydroxyl groups and the alkali of the glass in a way that the shrinkage of the glue under the influence of heat tears out pieces of glass rather than break at the glue-to-glass interface. This phenomenon has been used commercially for many years to produce a type of frosted glass."[4] For this particular application, glass could be too clean if the hydroxide layer had been removed.

Some neutral atoms and molecules are attracted to each other by virtue of polarization effects which give rise to the so-called Van der Waals forces. A spherically symmetrical electron cloud around an atomic nucleus on the average does not exhibit any polarity; nevertheless, at the moment when a valence electron is, say, at the left of the sphere, there will be a preponderance of negative charge on that side of the atom and a positive charge on the other side; a dipole moment thus exists which rapidly fluctuates. When two atoms approach each other sufficiently closely, their respective dipole moments will affect each other in such a way that the fluctuations in time are synchronized and produce a lowering of the potential energy of the system which is inversely proportional to the seventh power of the effective spacing between the two atoms. Quite apart from any other forces that may be present at the same time, this increment of negative potential energy, by definition, is equivalent to an attractive force.

When the electron cloud of an atom or molecule is nonsymmetrical to begin with, it has a dipole moment in a given direction. As long as the thermal energy causes rotation of the molecule, this polar direction will be smeared out over a sphere. At lower temperatures, this rotation ceases, and an oscillatory motion about equilibrium positions will result. Negatively charged ions at a surface will then attract the positive ends of such dipoles and initiate adhesion. Sometimes surface ions and adsorbates are not compatible, as is the case for silver and soda-lime glass. The established artifice of treating the glass first with tin compounds serves to build suitable ions into the surface which can interact with dipoles of silver.

Van der Waals forces are relatively weak in comparison to other bond types, but they can reach the strength of chemical bonds when large asymmetrical molecules are involved. The forces acting between layers of natural mica are of the Van der Waals type. The application of phosphor screens to the surface of picture tubes depends to a large extent on the selection of media which favor the action of complex surface forces.

Another area where bond mechanisms are of great technical importance is the production of reliable metal-to-ceramic seals. Such seals are being made commercially every day in large numbers, and different producers employ their most favored techniques without really understanding why they work. The art has progressed far beyond the science. This state of affairs is embarrassing because it leaves the way open to witchcraft. Fortunately, several large-scale investigations of this field have recently been sponsored by government agencies which, jointly with privately supported studies, begin to shed light on this maze of complex phenomena. It would lead us too far afield to attempt a discussion in detail of the many factors involved in the formation of a bond between ceramics and metals. In general terms, the ceramic surface is first metallized, and the metal member is then brazed onto this surface coating. When active alloys are used, both these steps are carried out in one operation. The result in each case is a thin interface which forms a bridge between ceramic and metal, similar to the oxide interface in a glass-to-metal seal but much more complex in structure. Most ceramics, except the pure oxides, contain a certain amount of glass, and the sintered metal powders are partially oxidized. Interdiffusion of glass and metal oxide is thus likely to play a role in the bond formation if a glass phase is present in the ceramic. If it is not, the addition of silica to the metallizing paste has been found most beneficial. Chemical reactions also play a part, and sintering of the metal powder coating to a dense layer is essential. To elucidate the relative importance of these several mechanisms is a very challenging task and requires the employment of very sophisticated techniques of analysis.

You may wonder by now, if you did not long before this, what this discussion of bond mechanisms has to do with your business. The last paper scheduled on this Symposium deals with the question: "What the Scientist expects from a glassblower today," and I would suspect that it will resolve your bewilderment. Unless you cultivate a lively curiosity in what the scientist is up to and not just execute automatically the designs which are handed to you, you miss a great opportunity. I don't mean to imply that you should be theoreticians as well as craftsmen; not at all. But you should work with your head as well as with your hands. Quite a number of advances in techniques have been made in recent years which any one of us could have proposed. Do we always allow our imagination to run freely and ask searching questions? To pose such questions requires at least some familiarity with the subject, and it is to this extent that I think you should strive to be informed. It also requires a special receptiveness of mind to note the unusual effects which occur at times during your work and make them the basis of speculation which may lead to new discoveries.

I have always enjoyed glassblowing because the results of one's efforts are immediately apparent; if successful, the article can be put to use. Application is thus the prime objective in most cases unless one thinks of the fabulous exhibit of glassflowers in Cambridge were aesthetic appeal and sheer beauty are an end in themselves. The satisfaction derived by a glassblower from producing an article may thus stem simply from his pride in having the necessary manual skill. On the other hand, he may take his skill for granted and be more interested in the use that is being made of his product. Or, having achieved something new in the art on the basis of searching questions about the nature of glass, he may treasure his better understanding above all else, regardless of any immediate practical application.

The scientist has similar multi-variant motivations for pursuing his work. The practical applications of his research have been over-emphasized in our time as they have been before. While we freely benefit from these applications and strongly depend on them, they have been of a very awesome nature of late. This makes us look on scientists with the same feeling that primitive peoples had toward the medicineman, "whom they regard as an individual essential to the group but who is feared and often hated." "The scientists themselves have a share of responsibility in this misunderstanding because they do not convey to the public the nobler aspects of the scientific heritage."[5] Only a very small fraction of our present expenditure for research goes to basic research (about 6 per cent), but this does not imply that the majority of our scientists who work on utilitarian projects have forgotten their calling, which is to search for new knowledge and understand nature. They really are quite ordinary human beings, quite aware of their failings, and they might even appreciate a little support from you, the glassblowers, from time to time.

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ALUMINO-SILICATE GLASSES*

F. L. Bishop
Kimble Glass Company

Most glassblowers have been familiar for many years with classes of glass compositions such as the soda lime silicates frequently called flint glasses; the borosilicates which are usually called under the term of hard glasses; and the lead-containing glasses, such as KG-12, which are nice, soft, easily worked glasses having relatively high resistivity compared to the soda lime glasses. In recent years, a new class of glass compositions has appeared, namely, the alumino-silicates. Generally speaking, these glasses are basically silica with close to 20 per cent alumina and most of the balance of the glass lime and magnesia.

For some years now, Kimble has offered EE-2 glass which is the basic composition of our group of alumino-silicate glasses. It is essentially an alkali-free and boron-free material consisting only of oxides of silicon, alumina, calcium, and magnesium. There are, of course, traces of soda and other elements which are inherent in raw materials or in furnace melting of glass, but these are extremely minor in quantity. It is well known that EE-2 seals to molybdenum. The Kimble alumino-silicates now include glasses for sealing to several other materials such as alumina and tantalum. We also have EE-4 glass which has practically the same physical properties as EE-2, but contains some cerium which reduces the amount of browning from the electron or X-ray sources.

There are many excellent reasons for using the alumino-silicate family of glasses. First and most obvious, of course, is the high temperature service. EE-2 having an annealing point of 755°C. (1392°F.) can actually be used in the form of a tube under vacuum at temperatures well above 700°C. Some other forms of alumino-silicates can be used up to 150° higher.

GLASS TYPE		AN.PT.	SOFT.PT.	WORK PT.	RES.AT 350°C
LEAD	KG-12	433	635	980	7.8
SODA LIME	R 6	520°C	700°C	985°C	5.2
BOROSILICATE	KG-33	555	820	1240	6.6
ALUMINO SILICATE	EE-2	755	955	1210	11.5
96% SILICA	(7900)	910	1500		8.1

Figure 1

Figure 1 shows a comparison of EE-2 glass with Kimble KG-33 and other well known glasses with their high temperature properties. Figure 2 shows comparison of the constituents of these glasses. We might point out that most of the constituents which have been eliminated from EE-2 but are present in the other glasses, are well known for their diffusion through glass and their poisoning of the various materials placed on the glass surface.

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*Patented Nov. 22, 1960 No. 2,961,328

GLASS TYPE		SILICA	ALUMINA	B_2O_3	LIME	ALKALIS	LEAD
SODA LIME	R-6	68	3	1½	11½	16	
BOROSILICATE	KG-33	80½	2½	13		4	
LEAD	KG-12	56	1½			12½	30
ALUMINO SILICATE	EE-2	61	19		20		

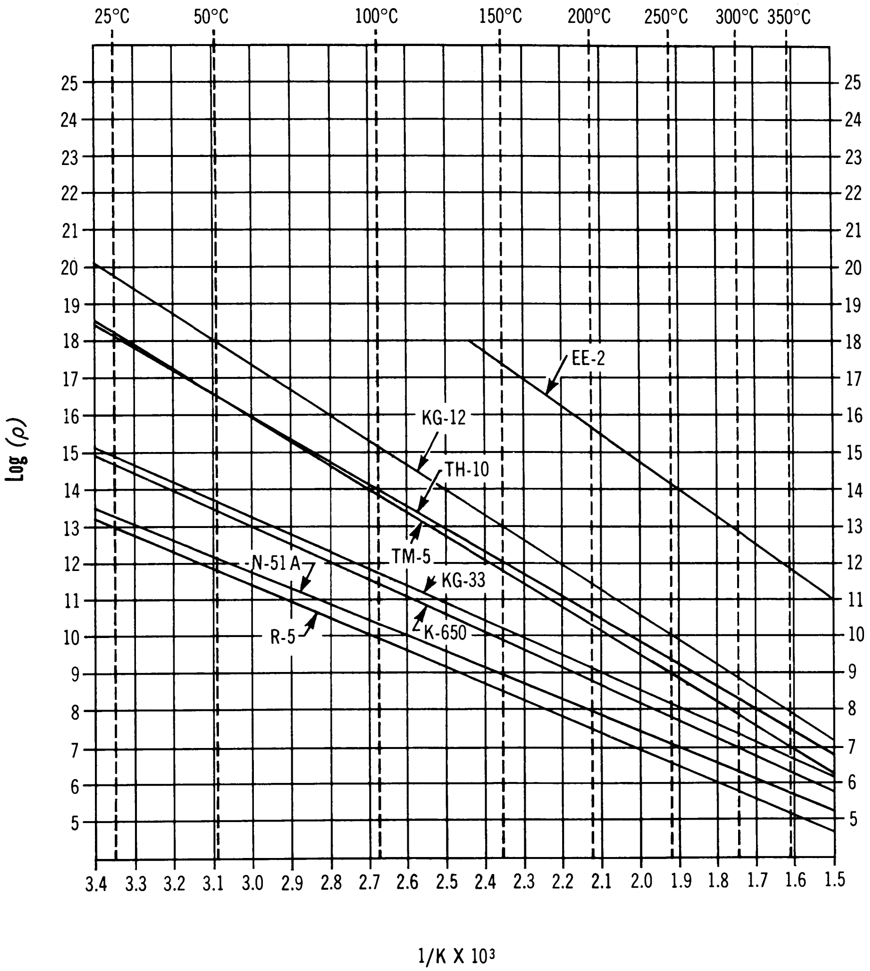
Figure 2

Tied in with the high temperature service of these alumino-silicates is the high electrical resistivity. On Figures 3 and 3a it is readily seen from the Resistivity-Temperature Curves that EE-2 is very superior in resistivity to any of the other common glasses in general use. I have included KG-12 which up to the present has been a standard of high resistivity glasses. All of the alumino-silicates have relatively high resistivity. I regret to say that at this time we cannot get both the high temperature bake-out characteristics and the low resistivity necessary in eliminating the breakage caused by charged build-up on the inside of extremely high-voltage electronic devices.

The next feature of the alumino-silicates which makes them outstanding is the low gas permeability. Figure 4 shows a comparison of the various classes of glasses, showing that the alumino-silicates are among the least permeable glasses known. The lead borate shown on this graph is representative of the solder glasses commonly used and the solder glasses used for alumino-silicates also have this extremely low permeation velocity. In addition to low gas permeation, the high temperature properties of this glass enable one to bake out electronic tubes and other items at temperatures approaching 750°C. This reduces the gas evolution from the metal parts in the tube much more than that encountered with other glasses where 450° to 400° is the standard bake-out range. In addition to the gases given off by metal and glass parts during operation of electron tubes, there are frequently constituents of the glass which evolve either because of electron bombardment or because of high temperatures. Also, in the sealing of glass parts you are all aware that it is necessary to make the seals carefully and uniformly or more volatile constituents will come from the glass to change its characteristics around the seal. This then leaves stresses in the seals. The alumino-silicate glasses, on the other hand, do not have any volatile constituents and when heated to high temperatures all of the constituents tend to volatilize very nearly at the same time. Thus in the case of alumino-silicates, the glass may be exposed to sealing temperature for as long as an hour and still seal consistently to another piece which is just freshly heated. The original purpose which Kimble had for EE-2 glass was its use in neutron fields where the neutrons are absorbed by such items as boron in the ordinary glass and cause destruction of the glass materials. The alumino-silicates have an extremely low cross section for neutrons and thus can be used where other glass would disintegrate. EE-4 is also stabilized against damage by electrons or X-ray and Gamma rays. Thus, wherever atomic radiation is a problem EE-4 should be specified.

Finally, the chemical durability and weathering resistance of the alumino-silicates are outstandingly good. These glasses are the equivalent of the glasses

RESISTIVITY-TEMPERATURE CURVES



PLOTTED CURVES	COMPARABLE CURVES
EE-2	
KG-12	EK-3
TH-10	TL-2, K-30, EN-1, K-704, K-772, KG-22
TM-5	TM-3, K-52, KG-1, TM-6, K-705
KG-33	
K-650	K-51
N 51A	KG-34, N-10
R-5	R-6

Figure 3

normally used for chemical service and durability and thus can be substituted for such glasses particularly where radiation fields may be a problem.

To summarize briefly, the alumino-silicates are characterized by good properties at extremely high temperatures, low gas permeability, high electrical resistance, resistance to radiation of various kinds, and also good chemical durability.

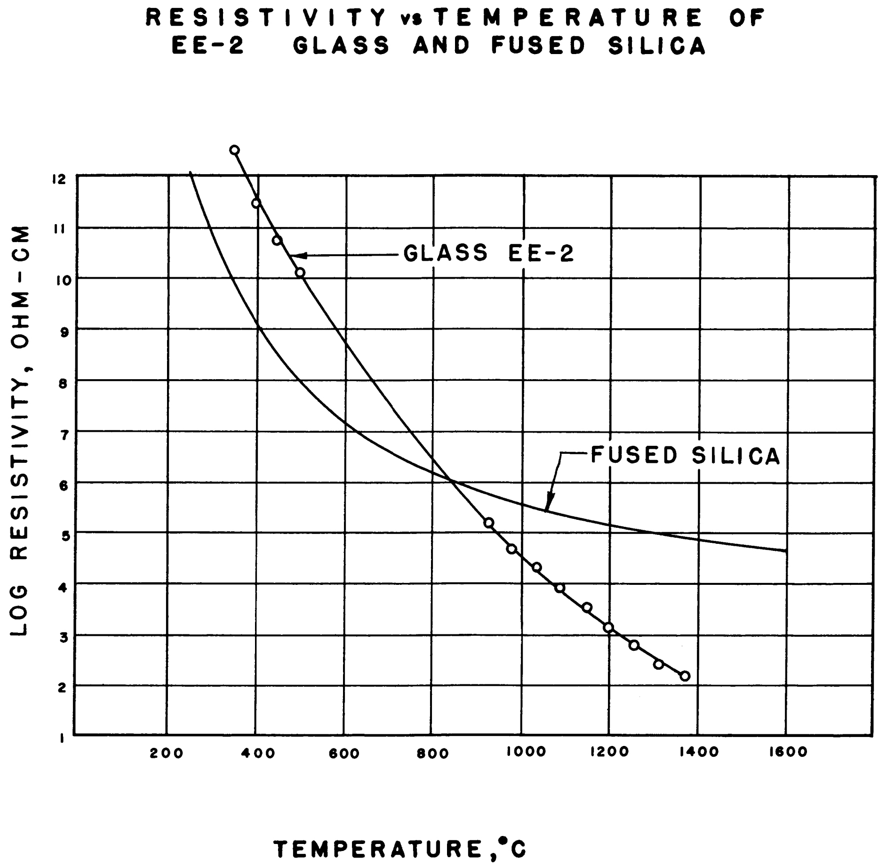
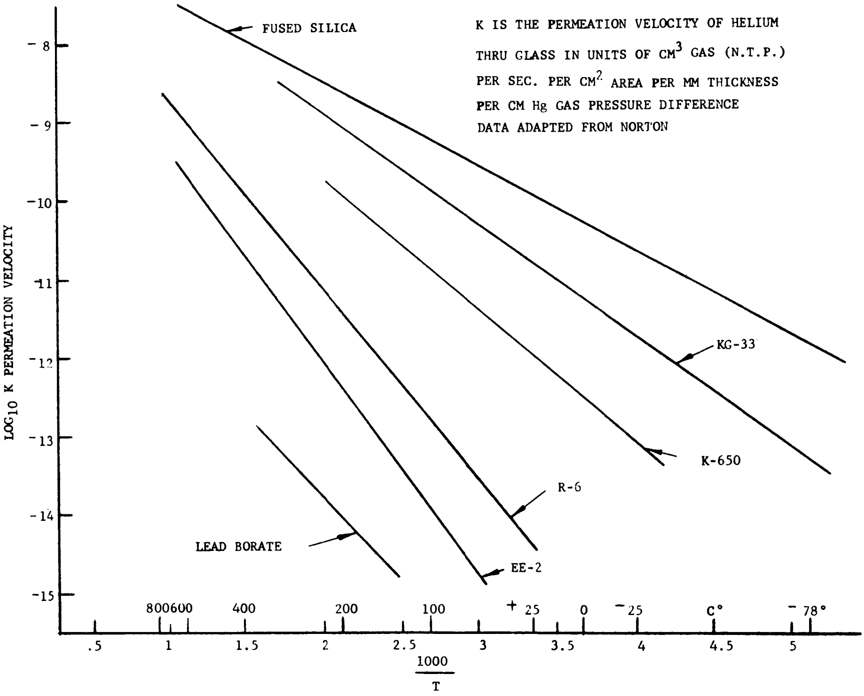


Figure 3a

KIMBLE GLASS COMPANY



K IS THE PERMEATION VELOCITY OF HELIUM THRU GLASS IN UNITS OF CM^3 GAS (N.T.P.) PER SEC. PER CM^2 AREA PER MM THICKNESS PER CM Hg GAS PRESSURE DIFFERENCE
DATA ADAPTED FROM NORTON

Figure 4

TECHNIQUES FOR LABORATORY WORKING OF ALUMINO-SILICATE GLASSES

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The alumino-silicate glasses offer unique properties, due to which they are finding increasing use as electron tube envelopes and in ultra high vacuum work. The combination of low coefficient of thermal expansion, high softening temperature, good electrical properties, low rate of diffusion of atmospheric gasses, and the ability to withstand considerable power loadings without seriously degrading vacuum would certainly lead to the more rapid and widespread acceptance of this class of glasses if they were readily workable by conventional and familiar techniques. These glasses have been extensively used in our laboratory for a number of years because of the exceptionally severe demands for ultra high vacuum conditions imposed by the sensitivity of field emission cathodes to contamination and sputtering.[1] While considerable difficulty was experienced during initial attempts, these glasses are now routinely worked by both flame and induction heating techniques. The versatility of this material, if properly handled, will be apparent from the accompanying figures.

In Figure 1 is shown an evacuation station during the pumping of several alumino-silicate experimental tubes. The entire visible glass structure including traps, manifolding, and gauge are of this material and are joined, through a Corning 3320 uranium glass grade, to a conventional cold trap and mercury diffusion pump of 7740 glass below the level of the table. By use of a muffle, the base of which is visible in the figure, and a protective atmosphere to avoid damage to exposed metal parts the system may be baked at temperatures up to, and slightly in excess of, the strain point of the glass. More specifically, temperatures to 680°C. have been employed.

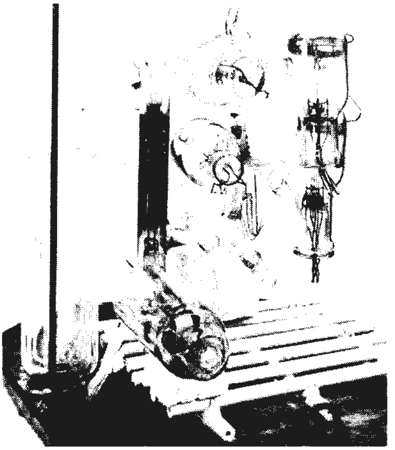

Figure I

Alumino-silicate evacuation station which may be baked to 680°C.

At the extreme left of the figure is shown a low impedance, self insulating, cold trap. Adjacent to the cold trap is a section of manifold containing a titanium evaporation filament which may be used to greatly increase pumping speed and to isolate the evacuating tubes from back-diffused chemically active gasses. The horizontally oriented component near the table level is a Redhead inverted magnetron gauge. This instrument has no demonstrated lower limit of sensitivity such as the "X-ray limit" observed in con-

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*Now at Field Emission Corporation, McMinnville, Oregon.

[1] For a brief discussion, see "Recent Techniques in Ultra-High Vacuum" by E. E. Martin and F. M. Collins, *Proceedings of 4th National Conference on Tube Techniques*, Sept. 1958 (N. Y. Univ. Press).

ventional, hot filament, ionization gauges, and is extremely useful at the very low pressures, of the order of 10^{-12} mm Hg, which are normally reached on this system. If the seal-off point is carefully heated and partially closed prior to the final bake cycle, it is normally possible to tip off the evacuated tubes with only a momentary increase in pressure to about 10^{-9} mm Hg.

Figure 2 shows a close-up view of the cold trap from the vacuum system of Figure 1, and is shown to illustrate the complexity of the structures which may be

Figure 2
Self insulating cold trap of alumino-silicate glass.

fabricated from alumino-silicates. Figure 3 shows an experimental switch tube. The tube elements are mounted on molybdenum leads pressed in an "X" configuration with a Litton Stem Head Lathe attachment. In Figure 4 is shown an experimental tube for measurement of the energy of field emitted electrons. A stainless

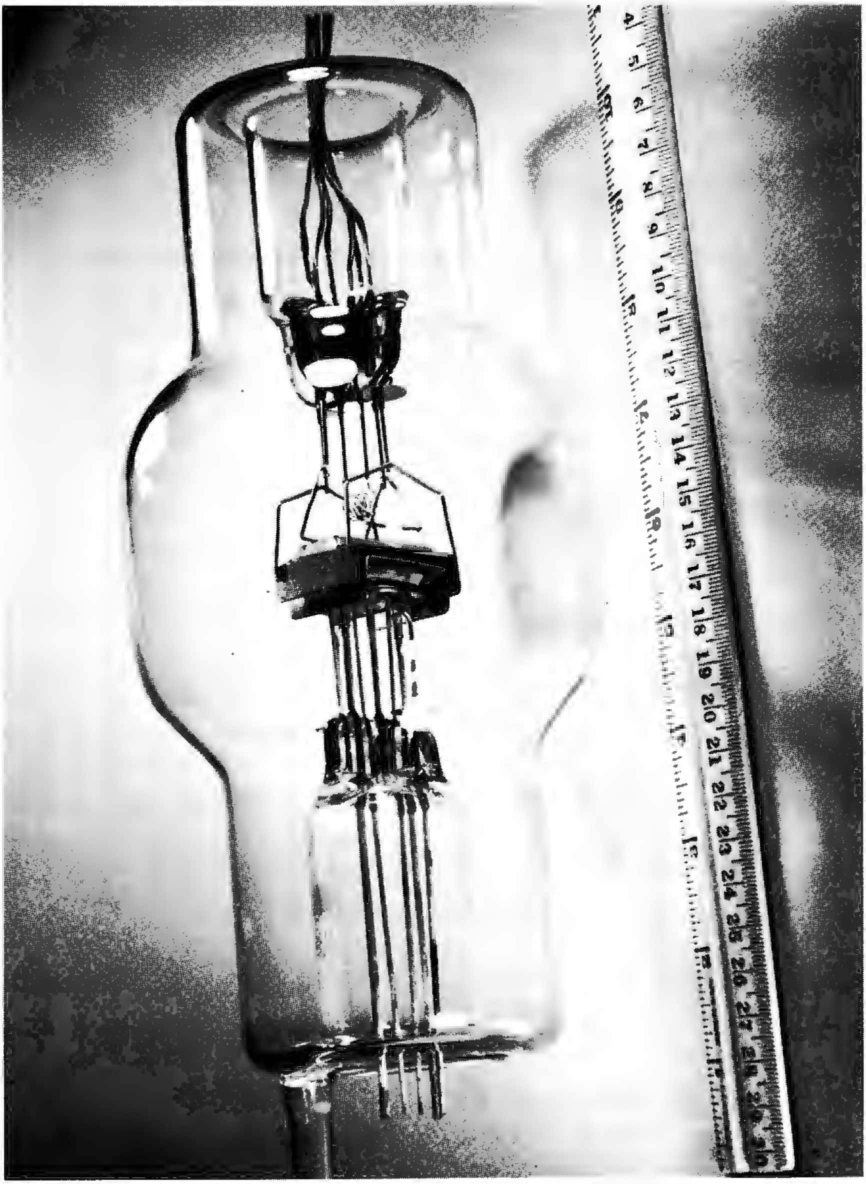

Figure 3
Experimental switch tube with alumino-silicate envelope.

steel bellows to permit adjustment of the cathode position is visible at the top of the figure and is joined to the glass through lengths of 1 inch diameter Mo tubing. The technique used in making such seals is discussed later in the text. A close up view of the internal structure of this tube is shown in Figure 5 and

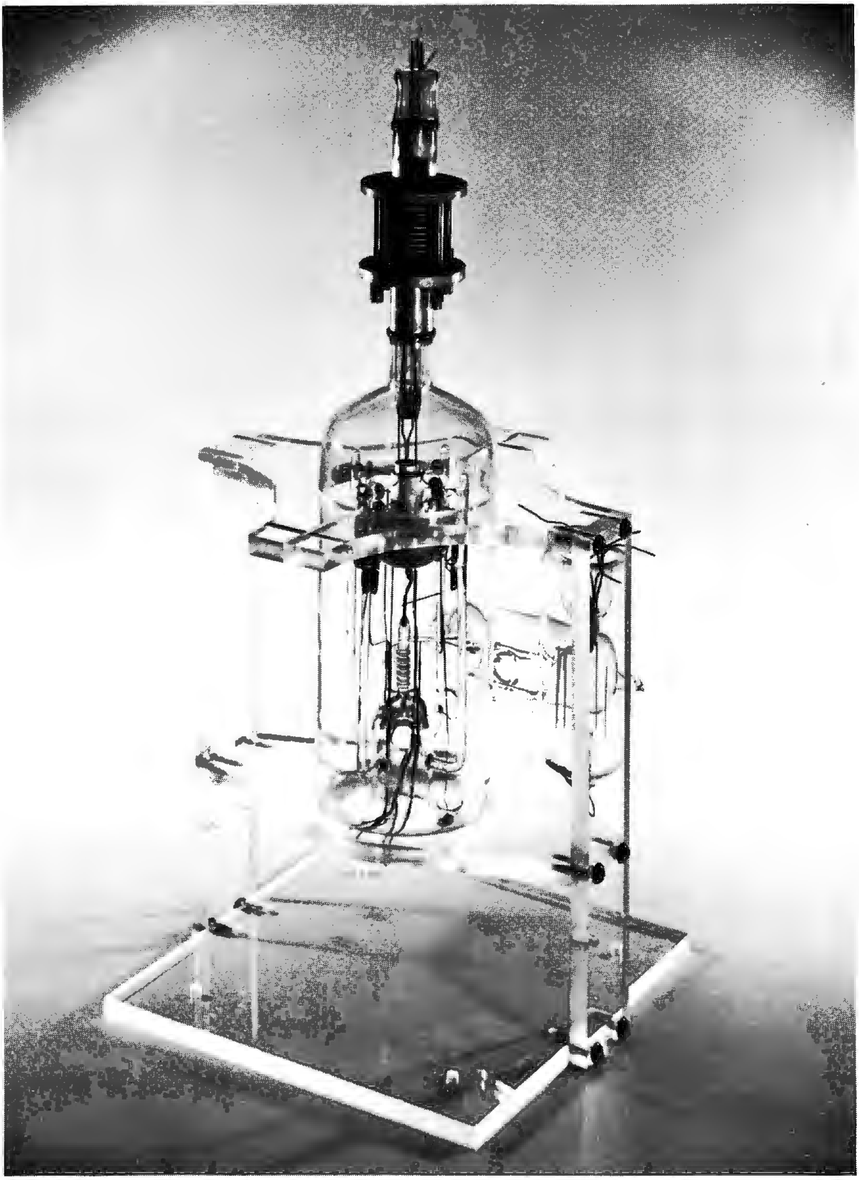

Figure 4

Experimental tube for study of electron energy distribution.

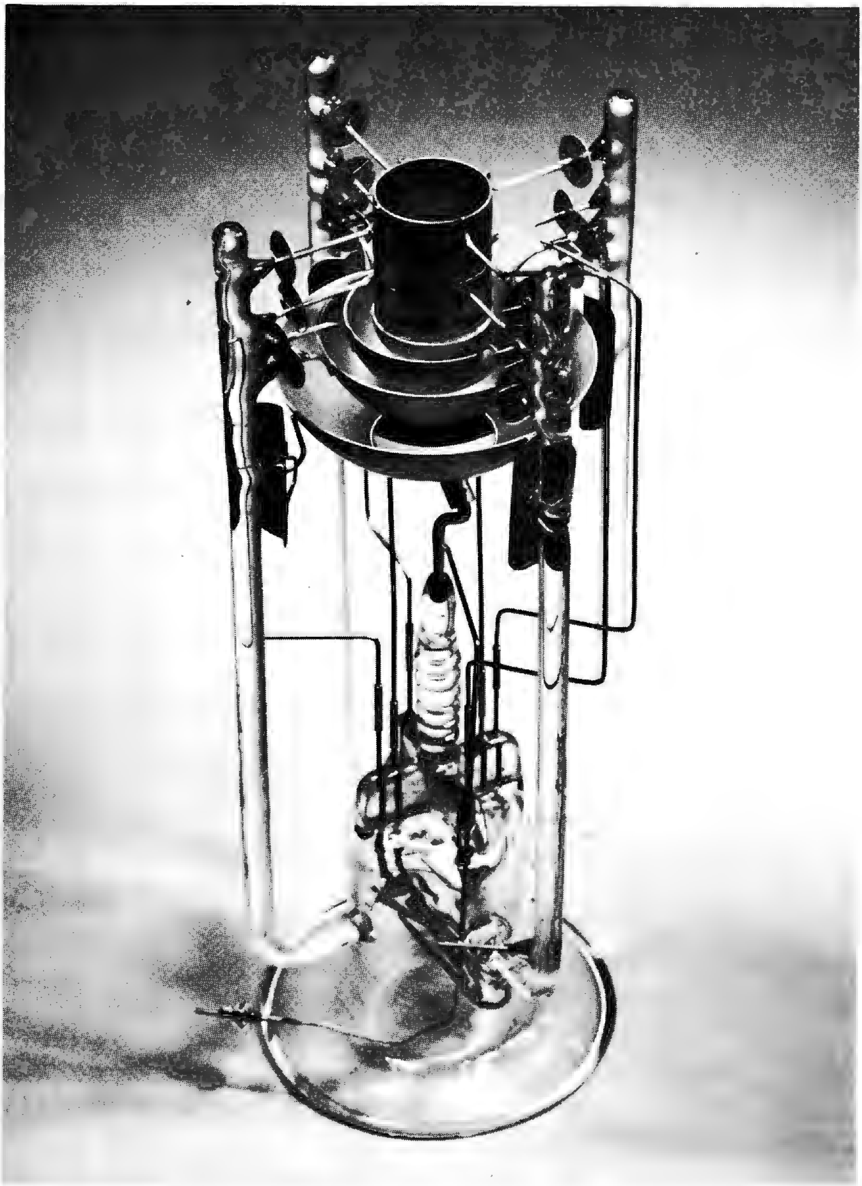

Figure 5

Lens structure mounted on alumino-silicate glass.

illustrates the use of alumino-silicate glass rods for the support of complex lens structures.

FLAME WORKING OF ALUMINO-SILICATE GLASSES

Cleanliness cannot be overstressed in the working of alumino-silicate glasses. All alumino-silicate should be cleaned both inside and out with alcohol or acetone before heating. Fingerprints, dust particles, or any foreign matter tend to cause reboil, *i.e.,* the release of gas and formation of bubbles near the surface of the glass, and should be removed. Use of carbon tools should be avoided if possible because the carbon tends to leave a deposit on the glass causing reboil. If it is essential to use carbon tools, they should be kept clean and replaced frequently. Burner jets should be free of residue also. In preparation for making seals or splices, the glass tubing should, whenever possible, be flame-cut rather than cracked-off because the mark left by the glass knife tends to cause reboil.

Most of our experience with alumino-silicate glasses has been with Corning 1710 and 1720 glasses. These materials are very similar in working characteristics and processes outlined herein are generally applicable to either material. Limited amounts of Corning 1723 and Kimble EE2 glasses have also been used; these materials were found to be more difficult to work than the Corning 1720, due to greater tendency toward flame reduction of metallic compounds.

In our laboratory these materials are normally worked without the use of flame additives; the needs for mixing equipment and the use of an exhaust hood are thus avoided. Conventional glassblowing methods are employed; however the type of flame used is very important. The glass may be pre-heated with a gas-air annealing burner, but actual working is done with a reducing hydrogen-oxygen flame. A torch which premixes gasses tends to cause less reboil and should be used whenever possible.

Most of our work is done in a glass lathe using Litton burners; hand work is done using a 6 burner cross-fire and a hand torch. Placement of the burners is important, and the distance from the fires to the glass should be greater than in working conventional glasses. Care should be taken to work the glass toward the tip or ends of the flame.

The following general steps for working alumino-silicate glass are used successfully:

1. All pieces of glass are cleaned inside and out with alcohol or acetone.
2. After chucking in the lathe, portions of the glass to be heated are wiped off again as a final precaution against fingerprints.
3. Larger sizes of glass are pre-heated using a gas-air annealing burner until the glass shows a golden color.
4. Following pre-heating, the lathe burners are lit, starting with pure hydrogen, and adding oxygen slowly until the working temperature of the glass is reached.

Care should be taken to have a bushy hydrogen flame and to add the oxygen slowly. Smaller glass sizes, 1 inch O.D. or less, do not require the gas-air flame pre-heating. As little oxygen as possible to still give sufficient heat for working the glass is added. When moving to a new area to work, even though it is adjacent to the previously worked area, the same pre-heating procedure is followed, that is, a bushy hydrogen flame is used and oxygen is added slowly until the working temperature is reached. Corning 1720 glass will reduce or darken slightly but not enough to cause difficulties. All 1720 glassware is flame-annealed with the gas-air burner or placed in a pre-heated oven and annealed at 720°C.

Flame mixtures were analyzed by means of flow meters in the hydrogen and oxygen lines. For flame working of Corning 1720 glass see the data in Table I. These data may be summarized by the generalization that a 5 to 1 ratio of hydrogen to oxygen is used whenever possible; a 4 to 1 ratio is used for work requiring greater heat, and a ratio as low as 3 to 1 caused only slight reboil. These observations are valid only if pre-heating is done with a pure hydrogen flame, and the oxygen content is added slowly.

TABLE I

1720 Glass Size O. D. (inches)	Type of Glass Work Done	Type of Burner	Distance from Burner to Glass (inches)	Flow Meter Reading Hydrogen Line (Cubic Feet per Hour)	Flow Meter Reading Oxygen Line (Cubic Feet per Hour)	Gas Ratios (H_2/O_2)
1/2	Tubing was heated and blown up to 1-1/2" in size	4 jet Litton Burner	1-1/2	56	11	5/1
1	Tubing was flame cut in the middle and spliced together again	4 jet Litton Burner	1-1/2	68	13	5/1
2	Tubing was heated and thickened then flame cut and flared to 3"	8 jet Litton	1-1/2	168	32	5/1
2-1/2	Tubing was reduced in size to 3/4"	8 jet Litton	1-1/2	185	38	5/1
3	Tubing was blown up to 5"	8 jet Litton	1-3/4	240	53	4/1
.054"-.066" Glass Tubing	.050" Mo. Rod was beaded	Cross fires 6 burner	4	206	46	4/1
With the flame gradually made more oxidizing, slight reboil was noted under the following conditions:						
2	Tubing was spliced	8 jet	1-1/2	92	28	3.3/1

Corning 1723 and Kimble EE2 glasses present more problems in flame working because they tend to reduce so badly that transparency is affected when worked with a highly reducing flame. The only successful way found to work these glasses without causing severe reduction was to pre-heat with a highly reducing hydrogen-oxygen flame until the glass started to reduce or darken, then enough oxygen was added so that the reduction ceased and transparency was restored. The glass could then be worked without causing reboil or reduction. Here the mixture is much more critical; not enough oxygen causes reduction, and too much causes reboil. Flow meter data for working Corning 1723 glass are summarized in Table II. It should be noted that in the case of 1723 glass it was necessary to reduce the ratio of hydrogen to oxygen to about 2.5 to 1 to avoid excessive reduction of metal oxides in the glass.

TABLE II

1723 Glass Size O.D. (inches)	Type of Glass Work Done	Type of Burner	Distance from Burner to Glass (inches)	Type of Flame	Flow Meter Reading Hydrogen Line (Cubic Feet per Hour)	Flow Meter Reading Oxygen Line (Cubic Feet per Hour)	Gas Ratios (H_2/O_2)
1/2	Tubing was heated and blown up to 1-1/2" in size	4 jet Litton	1-1/2	Preheating Flame	44	10	4.4/1
				Working Flame	44	15	3/1
1	Tubing was flame cut and respliced	4 jet Litton	1-1/2	Preheating Flame	50	12	4/1
				Working Flame	50	22	2.3/1

In our laboratory molybdenum is used to seal to alumino-silicate glasses, as it yields an adequate match of average expansion coefficients between annealing and room temperature. Usually it is nickel plated to prevent excessive oxidation. 0.050″ leads or pins are generally used and are wetted with a thin alumino-silicate glass bead before electroplating. We have had good success using this method, but chromalized[2] molydenum is more effective for the prevention of oxidation during glassblowing operations. We usually prefer the nickel electroplating method, however, because after the glass press seals or stems are made, the nickel plating is easily removed, and the molybdenum remains malleable enough to be bent, when necessary, without heating. The molybdenum leads which we use are obtained, with flexible strand attached, from Kulite Tungsten Corporation, Ridgefield, New Jersey. The molybdenum leads are ultrasonically cleaned in alcohol, flame oxidized, and then glass beaded; the color of the oxide layer beneath the glass bead should be dark brown. No hydrogen or vacuum firing is required prior to glassing. Following the electrolytic removal in sodium hydroxide of all oxide not shielded by the glass bead, the exposed metal is nickel plated. When using the nickelplating method it is essential to have a muffle-oven to prevent oxidation of the leads during annealing of the glass. Forming gas (90% N_2, 10% H_2) may be used as a protective atmosphere, both in certain glassblowing operations and in the muffle-oven.

For simple experimental vacuum tubes, where a small number of electrical leads are required, the standard flat press seal is used. In the more complicated tubes where many leads are necessary for both electrical connections and internal structure support, we have found "X" shaped presses made with a Litton stem head lathe attachment very useful. As many as twelve 0.050″ molybdenum leads have been pressed into a seal of this design. The "X" press design is excellent for both spacing of the leads and mechanical support of internal metal parts. In making headers, press seals, or stems the work is placed in the pre-heated muffle-oven immediately after completion.

When a vacuum system with 7740 glass manifolding is used, the tubes are sealed on using a graded glass seal from the pyrex to uranium glass (Corning 3320) to 1720. Using a system of this type, a high bake-out temperature cannot be reached, but, even with a 500°C. bake-out, alumino-silicate glass tubes can normally be evacuated with a shorter pumping time than tubes of more conventional materials because they tend to clean up more readily. In many instances, the time saved during evacuation more than off-sets any difference in fabrication and material costs.

In some instances tubes containing tantalum or titanium components have been constructed. Since annealing in an atmosphere containing hydrogen was not desirable in these cases, the most severe strains were removed by baking during evacuation at a temperature slightly in excess of the strain point, with a neutral atmosphere being used during the treatment to protect exposed metal parts. No distortion of the envelope by atmospheric pressure could be detected following baking for 2 hours at 680°C.; the structures were not completely strain free, but all sharp strains had been reduced to blanket type strains.

Tubular seals to ½ inch diameter between molybdenum and Corning 1720 glass are readily made by flame working techniques. Rounded metal edges, such as are used on Kovar to glass seals, are employed; the metal is flame oxidized in the

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[2] Hees and Earley, "The Use of Almino-Silicate Glasses in Experimental Vacuum Devices".

same manner as the leads for a press. As much hydrogen as possible should be used to avoid formation, and mixing with the glass, of volatile molybdenum trioxide. Tubular seals larger than ½ inch in diameter are more conveniently made by induction heating than by flame working.

SEALING OF ALUMINO-SILICATE GLASSES TO MOLYBDENUM BY INDUCTION HEATING

Because induction heating techniques permit greater control of the atmospheric environment, they are useful in a number of operations which would be difficult or impossible by flame working. Among the items fabricated from alumino-silicate glass by this technique in our laboratory are tubular metal to glass seals, fritted headers, microwave windows, tubular disc seals, and complete stacked-element electron tubes. Most of the work has been performed with Corning 1720 and 1723 glasses, and the techniques outlined in the following are applicable to both materials. Except for minor differences in the glasses and techniques, we have used the methods described by Hillier and Bell.[3]

Fabrication of tubular molybdenum-to-glass butt seals, such as the one inch diameter seal shown in Figure 6, are made with a drop jig which maintains alignment and controls the depth of penetration of the metal into the glass. The metal is prepared in the same manner as for a flame seal, *i.e.,* rounded at the edge and pre-oxidized. The glass tubing is prepared by flame cutting followed by heating and allowing the edge to thicken into a bead. The beaded edge should be thick enough and of proper diameter to permit glass to flow both inside and outside of the metal tubing. The molybdenum tube is mounted in a vertical position, with the prepared edge of the glass resting on it and held on a common axis by the jig. The entire structure is enclosed in a "Vycor," or, quartz tube and an inert atmosphere such as argon is admitted. When the molybdenum is induction-heated the glass in turn softens and is forced downward by the weight of a movable portion of the jig, the travel of which can be accurately limited. Sharp strains are subsequently removed by controlled-atmosphere oven annealing.

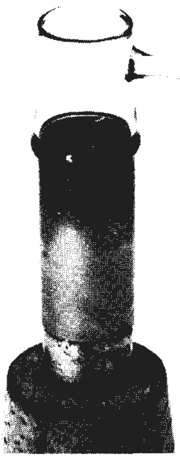

Figure 6

Alumino-silicate to molybdenum tubular butt seal.

In fabrication of tubular disc seals to flat molybdenum plates the glass is first cut into the desired lengths on a wet cut-off wheel. Tubing segments should be longer than the desired final dimension by an amount about equal to the wall thickness, in order to provide for glass flow on the metal surface. The area of the glass to be sealed is dipped in concentrated

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[3] M. Hillier and R. L. Bell, *Brit. J. Appl. Phys.* 9, 94 (1958).

hydrofluoric acid to etch the surface and remove any traces of abrasive that may be imbedded in the glass. This is followed, after thorough rinsing in running water, with ultra-sonic cleaning in a detergent solution. The glass is finally rinsed in four alcohol baths and allowed to dry in air before use.

The molybdenum component that is to be sealed to glass is electrolytically polished in a phosphoric acid solution and then electrolytically etched with alternating current in sodium hydroxide to produce a satin finish. The part is ultrasonically cleaned in a detergent solution, then rinsed in running water, and immersed successively in four alcohol baths. The metal is pre-oxidized by rf induction heating of the part in air to approximately 1000°C. Proper oxidation is evidenced by observing either the color brightness or noting the evolution of the volatile, yellowish white, trioxide of molybdenum. Following oxidation, the part is heated in an inert atmosphere until all traces of the trioxide are evaporated. The oxide layer should have a uniform reddish-brown appearance.

The glass-to-metal seal (Fig. 7) is made in a boron nitride jig that has been designed to allow the desired fall for the disc and also to maintain concentricity of the components. The metal disc is heated with rf in a flux concentrator at approximately 1000°C. until the disc has fallen the desired distance. The temperature of the work is then increased to 1200°C. until the metal disc has been wet by the glass. The degree of wetting may be judged by the contact angle; for reliable seals the glass surface should make an acute angle with the metal surface.

An envelope requiring several discs in a stacked array is fabricated from several "sandwich" units. These units consist of two metal plates separated by the desired length of glass. They are then brazed together in a reducing atmosphere

Figure 7a
Alumino-silicate to molybdenum tubular disc seal.

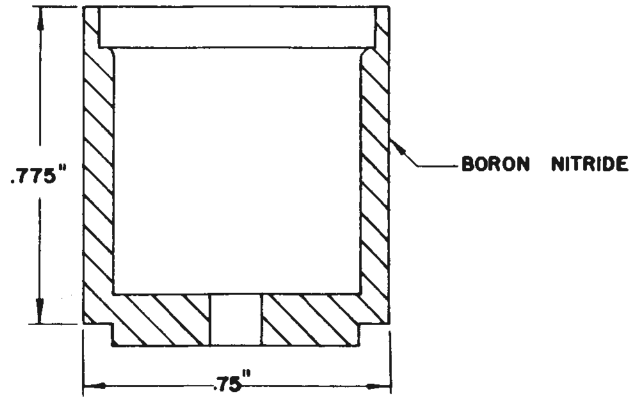

Figure 7b
Boron nitride jig used to make disc seal.

furnace. In our laboratory, gold-nickel eutectic braze material is commonly used for this purpose. It is possible to seal glass cylinders to both surfaces of a metal disc, however, the more complicated jigging then required makes the fabrication and brazing of "sandwich" units more economical, and equally reliable envelopes

Figure 8
Alumino-silicate frit header with molybdenum pins and exhaust tubulation.

are obtained by either method. The brazing operation serves also to anneal the glass.

Another item utilizing rf sealing techniques which is fabricated in this laboratory is a microwave waveguide window. The window can be brazed into a thin walled section of copper waveguide and is capable of withstanding repeated bake out at 650°C. during evacuations.

Frit glass headers (Fig. 8) from 1720 glass are made by placing the desired amount of frit into a high quality carbon mold that is weighted sufficiently to cause the glass to flow when it is heated to approximately 1200°C. Frit size will vary according to the dimensions of the header. For headers approximately ½″ in diameter, frit which passes a 100 mesh screen works very well. Flame prebeaded molybdenum wires are sealed into the header during the forming operation. As many as five 0.050″ molybdenum pins have been sealed into a header that is 0.040″ in diameter. An exhaust tubulation may be formed as an integral part of the header. A tapered monel pin is used as the center mold for the tubulation. The frit will not seal to the monel which, when cool, can be easily extracted from the header. Such a header is sealed into the tube by heating a small carbon ring that is placed adjacent to the area to be sealed. (Figs. 9A and B) Surface tension forces cause the heated glass to collapse onto the header. A jig used for fabrication of headers is shown in Figure 10.

Figure 9a

Frit header sealed into alumino-silicate glass tube.

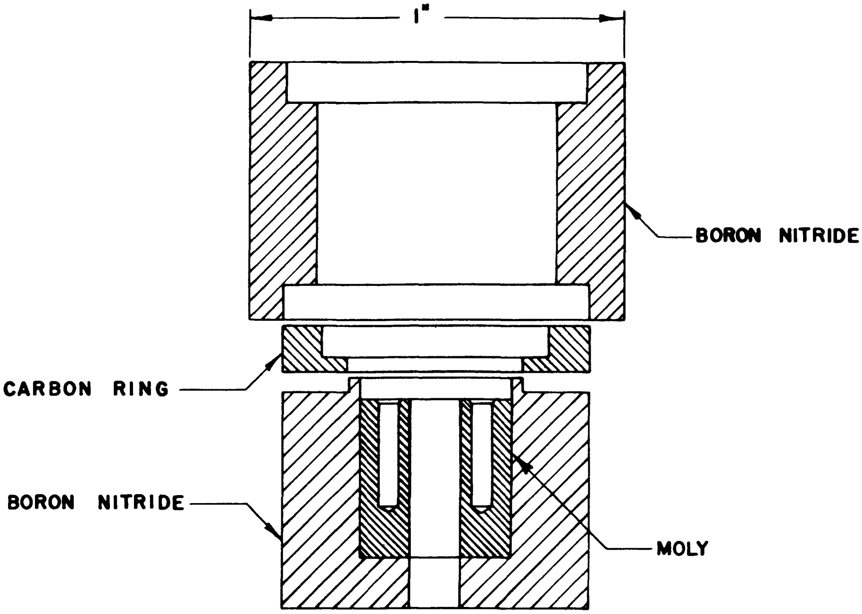

Figure 9b
Frit header sealed into alumino-silicate glass tube.

RF techniques make possible the fabrication of small vacuum envelopes of excellent quality, with metal parts that are easily prepared by stamping, and with a minimum of other hand labor. Reproducibility is excellent, and tolerances can approach those achieved with ceramic structures.

Acknowledgment

The authors are pleased to express their gratitude to E. E. Martin of Linfield Research Institute for continued interest and guidance provided during the development of the techniques described and for critical reading of the manuscript.

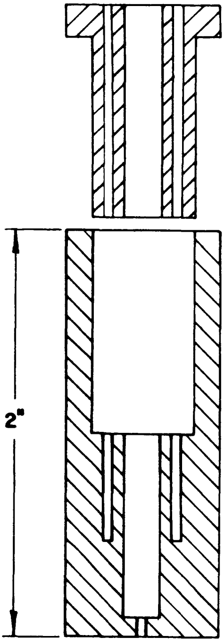

Figure 10
Carbon jig used to fabricate frit headers.

PROPERTIES AND APPLICATIONS OF DEVITRIFYING SOLDER GLASSES

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I. INTRODUCTION

Whereas the stable or thermoplastic solder glass has been with us for some time, the devitrifying or thermosetting type is of more recent origin. Just as devitrification in glasses was carefully avoided for many years until it was found that materials with desirable properties could be produced by controlled nucleation, so also in solder glasses, devitrification was avoided. In the controlled nucleation of glass ceramics, the objective is usually to thoroughly crystallize the body with a minimum of distortion. In devitrifying solder glass, one is dealing with much lower glass viscosities because the powdered glass must sinter together and flow to some extent in order to accomplish its mission. In addition, as will be seen, devitrification may or may not be extensive. Some useful devitrifying solder glasses end up with a rather large glassy content. Since one is always dealing with powdered glass applications, surface devitrification plays a much more prominent role than in glass ceramics.

In all cases the initial material is a glass. It has a typical glass-like expansion curve and its viscous properties can be described by the usual viscosity points: namely, softening point, annealing point and strain point. However, these properties cannot always be measured by conventional means.

In this paper the advantages and disadvantages in using devitrifying solder glasses will be pointed out, the properties of materials which have been released to date will be described, and other areas where the devitrifying solder glasses may have application will be indicated. Lastly, some of the general problems of solder glass application will be discussed.

Before going further, a few terms should be defined. The expansion of glasses is generally described by giving their linear expansion coefficient. This is measured (usually 0 - 300°C.) in the lower temperature range where it is quite linear. Actually, of course, in any sealing application the important expansion is the expansion to the setting up point. However, for most glasses the expansion to set point is a relatively similar fractional increment over the low temperature expansion (about 15%). Therefore, bearing this in mind, glasses can be classified quite well by using measurements over the same convenient interval in all cases.

Some confusion enters when glasses are compared with other materials like metals, alloys, ceramics or devitrifying solder glasses. Except for pure metals and some ceramic materials which have rather linear expansions to elevated temperatures, the expansions measured over a low temperature interval is of little value. To get anywhere in estimating compatability for sealing, a complete expansion curve must be used; and, in addition, the effective setting up point of the seal combination must be known. The yardstick of expansion mismatch is now the total differential to room temperature. This is usually expressed in parts per million and is identical with the units which most often appear as ordinates in a complete expansion curve. Practically, it is often convenient to estimate expansion match by measuring the stress developed in a test seal by stress-optical means.

To be useful, a solder glass should exhibit some flow when heated to the sealing temperature. Some seal configurations require much more flow than others. Of course, wetting of the seal surfaces by the solder glass is also very much influenced by the solder glass viscosity. We have evaluated glasses in this respect by pressing a given weight of solder glass dry in a ½" diameter mold. The pellet is then transferred to a suitable support and put through the same temperature cycle as would be used in sealing.

II. DEVITRIFYING SOLDER GLASSES VS. STABLE SOLDER GLASSES

A. *The advantages of devitrifying solder glasses are:*

1. Greater rigidity at high temperatures after sealing. This is the principal feature of the #95 Pyroceram Brand cement in the color TV tube application. Here, sealing is at 440°C. with subsequent exhaust bake as high as 420°C. with no relative movement of the parts.

2. Lower effective expansion for a given seal temperature. With stable solder glasses it is always true that a lower effective expansion can be obtained only at the price of an increased sealing temperature. Some reversal of this tendency is obtained by using devitrifying solder glasses.

3. Expansion characteristics may be more desirable. For instance, in some cases it is possible to maintain a compression stress in the solder glass at all temperatures between the sealing temperature and room temperature. This is not possible with stable solder glasses because contraction in the setting up region is always higher than that of bodies being sealed.

4. Lower fillet stresses. This is one of the less obvious advantages. A detailed discussion is beyond the scope of this paper; however, fillet stresses are those stresses that are brought about by viscous displacements in the solder glass during the cooling cycle in response to forces produced by differential contraction between the sealing glass and bodies being sealed. With stable solder glasses quite high differential contractions occur in the annealing range. Some devitrifying solder glasses are essentially set up during the sealing cycle so no viscous displacement occurs during the cooling cycle. In others, where complete setup does not occur in the sealing cycle, contraction rates in the setup region are often much lower than with stable solder glasses and so fillet stresses are lower.

B. *Limitations of Devitrifying solder glasses.*

1. Sufficient flow for good seal formation is sometimes hard to obtain. All the flow for good seal making and for developing an adherent bond to materials being sealed takes place in an early portion of the sealing cycle before the solder glass sets up enough to impede viscous flow. Poor flow cannot be counteracted by merely increasing the sealing temperature since this will usually bring about a faster devitrification and, therefore, little or no net gain.

2. Glass quality control is considerably more difficult than with stable solder glasses. Not only is the composition more critical but there are also greater possible variations in properties due to melting conditions, quenching methods, state of grind, contamination and weathering of the powdered glass. Inhomogeneities

as, for example, any slight crystallization occurring in cooling the melt to room temperature can have a great effect on the rate of devitrification of the powdered glass in sealing operation.

3. Sometimes it is advantageous to preglaze parts to be joined. With devitrifying solder glasses there is only a narrow range for sintering before the onset of devitrification so close temperature control is necessary. The difference in effective expansion between the glass in the vitreous and the devitrified state also creates problems. In some systems the difference in effective expansion between the glassy state and the devitrified state is so great that preglazing is not at all feasible.

4. Sealing is limited to powder glass methods. Former particle boundaries in the sintered glass serve as nuclei for crystal growth. Massive glass applied as preformed cane or sheet does not devitrify in a uniform manner. Preglazing by applying a stream of molten glass likewise is not feasible.

5. The seals are always opaque whereas seals made with stable glasses can be transparent or not depending on the method of application.

III. #95 PYROCERAM BRAND CEMENT

The #95 PRYOCERAM Brand Cement is the devitrifying solder glass that was developed for sealing color TV bulbs together. It has since found a variety of applications many of which we are no doubt unaware. Essentially, it is a glass with a softening point of about 375°C. which is quite stable at temperatures below 400°C. At 440°C. it undergoes devitrification which is essentially complete in one hour. After devitrification its effective viscosity is greater than the annealing point viscosity (10^{13} poises) so little or no flow occurs in the sealed joint on cooling. The color TV bulb is exhaust baked at temperatures as high as 425°C. with no relative displacement of the parts.

In Figure 1 the expansion curve of both the devitrified and undevitrified glass is given together with glasses that might be sealed with it. The effective annealing and strain points are also indicated. These values are inferred from deformation experiments and so may not be as precise as corresponding viscosity measurements on glasses using the fiber elongation method. The lowering of the effective expansion in devitrification is quite obvious here. Actually, the effect is somewhat greater than indicated because there is usually some residual stress in the solder glass which is apparently due to a volume expansion in the devitrification process. This effect is often observed in studying seal stresses in a furnace by stress-optical means.

It is generally felt that a somewhat lower expansion solder glass than corresponds to a match is to be desired since this would correspond to compression in the solder glass. Because of the shape of the expansion curve a small amount of mismatch in this direction at room temperature is sufficient to maintain a compressive stress in the solder glass at all temperatures in the cooling cycle and subsequent heating cycles.

The #95 cement is useful for sealing to glasses with expansions as low as 90.* With Code 0120 and Code 9010 glasses and complete devitrification of the solder glass the match at room temperature is very close.

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*All expansion coefficients are in units of: x 10^{-7} cm/cm/°C.

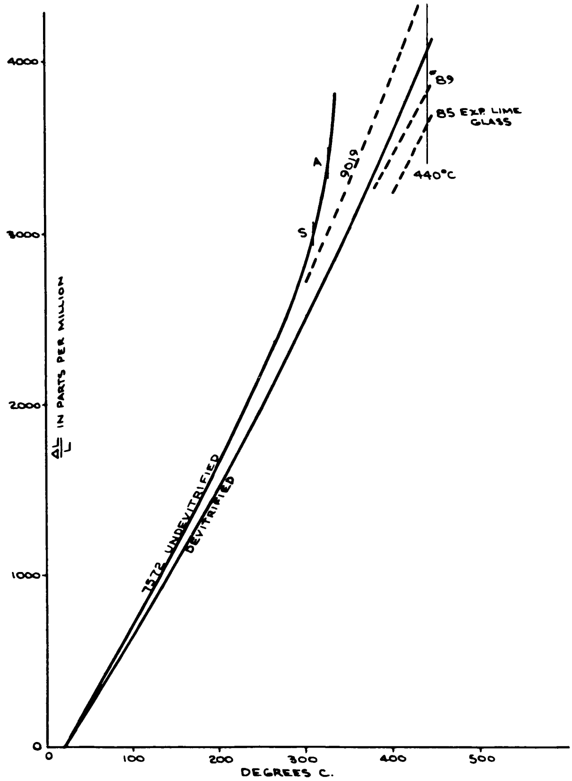

Figure I
Expansion curve for devitrified and undevitrified Code 7572 (PYROCERAM Brand Cement #95). Letters A and S on undevitrified curve indicate annealing and strain points respectively. Also indicated are portions of expansion curves of PYROCERAM Brand Cement #89, Code 0129 glass and a typical lime glass of 85 x 10^{-7} cm/cm/°C. (0-300°C.) expansion.

To provide a little better safety factor with Code 0120 and lime glasses, that is, a definite compression in the solder glass and a more favorable condition in cases where devitrification is not complete, the #89 PYROCERAM Brand Cement was developed. This can be processed under the same conditions as the #95 Cement and has a somewhat lower expansion. With it, seals to lime glasses with expansions as low as 85 are possible.

IV. #45 PYROCERAM BRAND CEMENT

With the successful application of the #95 PYROCERAM Brand Cement it was natural to consider extending the devitrifying principle into lower expansion ranges. Some work in this direction had already been done with stable solder glasses. With decreasing expansion the minimal softness increased thus requiring higher and higher sealing temperatures. When the expansion is lowered to the Kovar or tungsten expansion range there is relatively little advantage in solder glasses. An exception is the aluminosilicate glasses such as Codes 1720 and 1723 where the annealing range is considerably higher. Actually, one of the first solder glass experiments at Corning was the sealing of Code 1720 using a relatively soft tungsten sealing glass (Code 7750).

One of the hopes was that by applying the devitrifying solder glass principle some reversal in the general tendency of increased hardness with lower expansion might be brought about.

Attention was concentrated on a solder glass for aluminosilicate glasses. Devitrifying glasses with low enough effective expansions and with sealing temperatures in an acceptable range were soon obtained. However, a considerable amount of composition research was required to develop a composition which had adequate flow. The result of this investigation is Corning's #45 PYROCERAM Brand Cement.

This is a glass, with an expansion of 42 and a softening point of 640°C., which seals and devitrifies in one hour at 750°C. It does not contain easily reduceable components and so has application in neutral or slightly reducing atmospheres. The devitrified material has more glassy phase than the #95 Cement and so is not rigid at the sealing temperature but sets up at about 680°C., not far from the setup point of Code 1723. An appreciable decrease in effective expansion occurs on devitrification as shown in Figure 2. Here a comparison is made with Code 1723, PYROCERAM Code 9606 and Code 7740. It is interesting to note that due to expansion curvature a good match to Code 7740 glass, which has an expansion of only 32, is obtained. In this case, the solder glass sets before the Code 7740 on cooling. Of course, the processing temperature is too high for general application with Code 7740. Seals with suitably supported glass parts are none the less possible.

In regard to metals it matches tungsten quite well and can be sealed to molybdenum in many configurations. Because its setting point is well beyond the inflection point of Kovar, it would appear to have no application for Kovar sealing except perhaps for compression seals with Kovar exterior members.

With respect to Code 1723, there is a fair compression mismatch which is generally desirable. At the same time, the match between Code 1723 and the undevitrified glass is good enough to permit preglazing. For some applications, it is quite desirable to apply the #45 Cement using an organic vehicle and to preglaze parts in an air atmosphere prior to final assembly of parts for firing in a neutral or protective atmosphere.

Getting back to molybdenum sealing, for radial type geometries there is some indication that the #45 Cement may have too low an expansion. For this situation we have developed a higher expansion material having the same general character as the #45 Cement. It will also seal Code 1723; however, preglazing is not possible.

For a cement to be used largely for electrical applications with low loss materials there is interest in electrical properties. The high temperature resistivity of the #45 Cement is quite good, actually somewhat better than Code 1723. In Figure 3, the temperature at which the loss tangent reaches 0.5% is plotted against frequency for a number of materials. At microwave frequencies, dielectric properties are relatively good. Loss tangent at 8.6 Kmc is .002 with a dielectric constant of 5.8.

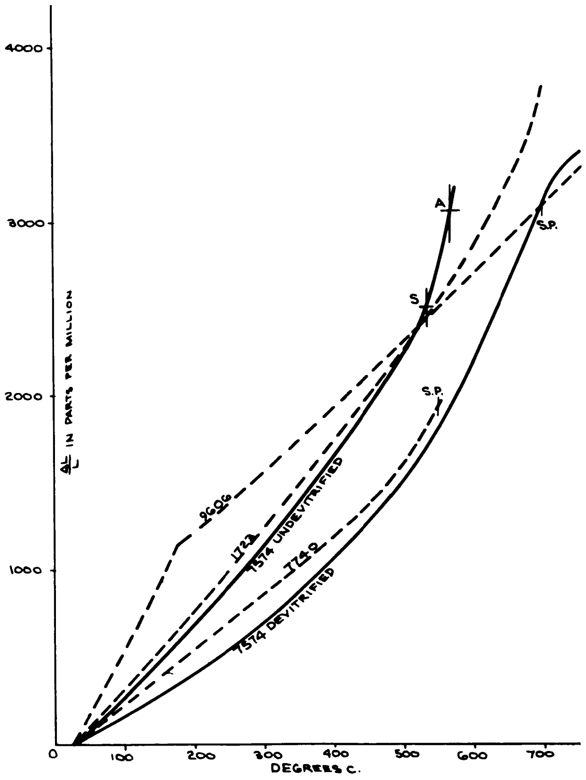

Figure 2

Expansion curve for devitrified and undevitrified Code 7574 (PYROCERAM Brand Cement #45). Letters A and S on undevitrified curve indicate annealing and strain points respectively. Letters S.P. on devitrified curve indicate approximate setting up point. Also given are curves for Codes 1723 and 7740 glasses and Code 9606 PYROCERAM.

V. OTHER SOLDER GLASS SYSTEMS

As can be seen, two basic sealing materials have been developed (#89 being considered as a modification of the #95 Cement). A logical extension of the devitrifying solder glasses would appear to be a glass for sealing Kovar. Kovar is one of the most versatile of sealing metals. It can be formed into a wide variety of shapes. It has been sealed into glass in almost every conceivable configuration. This success is a result of its curved expansion characteristic which matches certain glasses reasonably well, particularly in the annealing range. On the other hand, Kovar can hardly qualify as a high temperature material because of the pronounced inflection in its expansion curve starting at about 450°C.

Some progress has been made toward a solder glass for sealing Kovar to commercial Kovar sealing glasses such as Codes 7052 and 7056. The glass initially has an expansion of 85 and a softening point of about 510°C. After sealing at 600°C. for one hour or at 620°C. for one-half hour the material matches Code

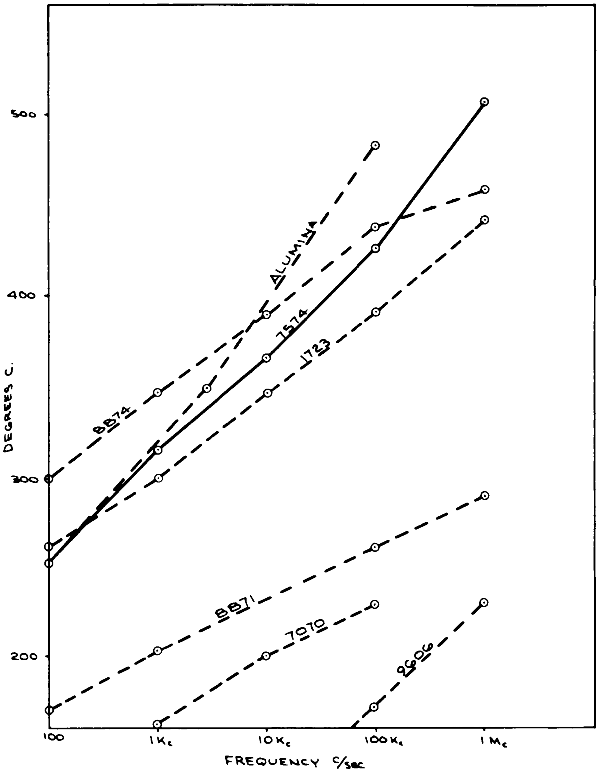

Figure 3
Temperature at which loss tangent reaches 0.5% as a function of frequency for a number of glasses, Code 9606 PYROCERAM, devitrified Code 7574 (PYROCERAM Brand Cement #45) and an electrical grade alumina body.

7052 glass quite well. There is indication of a relatively large amount of glassy phase in the devitrified body since the effective annealing point of the cured material is only 449°C. This is not much greater than the 432°C. annealing point of the original glass. Expansion curves for this material in both glassy and devitrified state are given in Figure 4. In Figure 5 a portion of this chart has been expanded to better indicate expansion match to a variety of materials. Of particular interest is Code 1723 and PYROCERAM Code 9606 which cannot be sealed to Kovar and are not compatible with Code 7052 when directly sealed. The principal use for such a solder glass may be for joining such diverse materials rather than sealing Kovar to Kovar sealing glasses.

It can be seen that there is a very large change in effective expansion in going from the undevitrified state to the devitrified state. This will of course preclude preglazing. It also spells disaster if the sealing temperature is too low or sealing time too short. Fortunately, underfiring can be recognized by the color of the frit which will be much too orange if underfired.

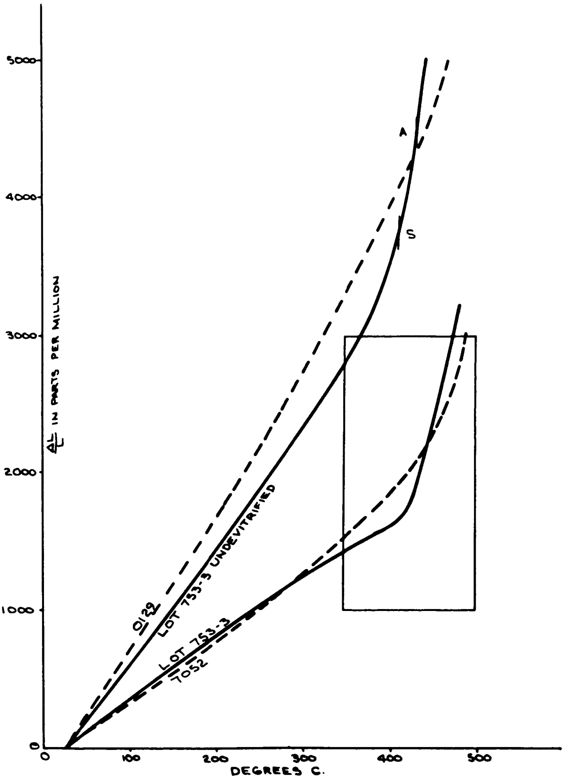

Figure 4

Expansion curve for devitrified and undevitrified experimental solder glass Lot 753-3. Letters A and S on undevitrified curve indicate annealing and strain points respectively. Also indicated are expansion curves for Code 0129 (98 expansion color TV funnel glass) and Code 7052 (Kovar sealing glass). Area within rectangle expanded in Figure 5 to better indicate expansion match to a number of materials.

As might be suspected from its low softness this glass contains reducible oxides and must be fired in an oxidizing atmosphere. Application is much the same as for the other devitrifying glasses. However, flow is not as good as with the #45 Cement.

Although the material is quite capable of sealing Kovar at temperatures which are not unreasonable for Kovar sealing glasses, there is another unrelated factor which will limit its use. With few exceptions Kovar seals are pickled to remove oxide scale and plated before ultimate fabrication into a device. Solder glasses are not noted for their durability toward strong acids and alkalies and this glass is no exception to the rule. No definite plan has been developed for marketing such a Kovar sealing frit. Action will depend largely on consumer interest.

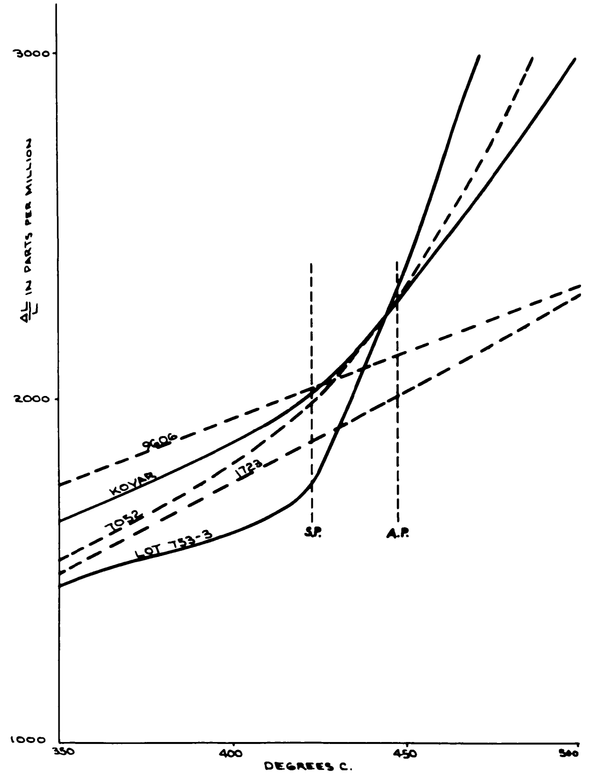

Figure 5

Expanded section of portion of Figure 4 to better show sealing compatibility. Letters A.P. and S.P. indicate effective annealing point and strain point for the devitrified Lot 753-3. Also given are expansion curves for Kovar, Code 7052 (Kovar sealing glass), Code 1723 (aluminosilicate glass) and Code 9606 PYROCERAM.

Obviously, there are other areas where devitrifying solder glasses might find application. One is a high expansion area above the range of #95 PYROCERAM Brand cement. Another possible area is in the 70 expansion area for joining glasses, alumina ceramics, and the newly developed Fernico V alloy.

VI. APPLICATION METHODS

Perhaps a few words should be said about application techniques. The limitation of the devitrifying solder glass technique is largely in physically filling the desired seal area with sintered solder glass. Some practical and some impractical seal geometries are shown in Figure 6. It should be remembered that there is a considerable shrinkage in going from a powder application to the sintered state. Preferably, a movement of parts should be available to take up some of this slack. This is provided in the butt seal geometry (A) and in the taper seal (B).

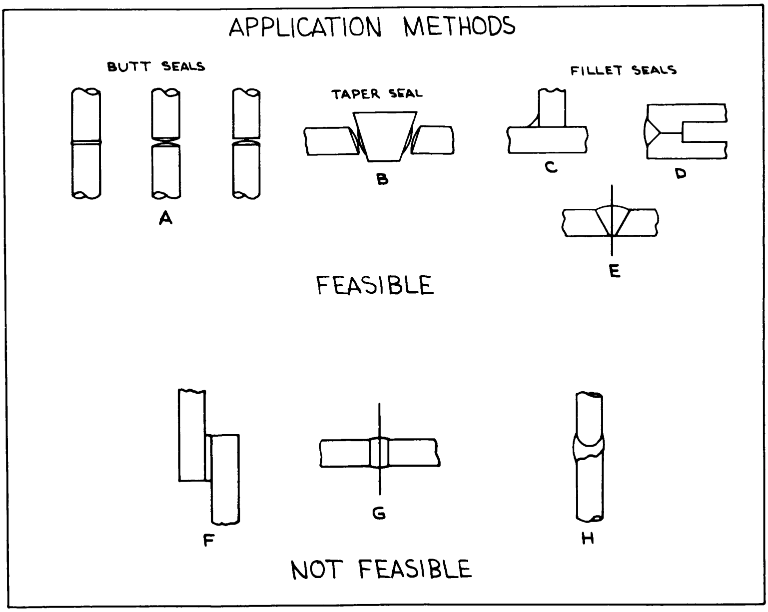

Figure 6
Some typical seal sections. Letters A, C, D, E and H may be considered as sections of cylindrical or rectangular elements.

In the butt seal, the solder glass can be applied to one surface, both surfaces, or the parts can be joined with the wet slurry. Application to both surfaces to be joined is generally recommended. With application on one surface, a very good solder glass flow is necessary to produce a good joint. The joint with wet slurry is useful where the solder glass doesn't have good enough flow to seal with separate frit applications.

Fillet seals (C, D, E) are more feasible with devitrifying solder glasses than with stable solder glasses.

In a seal such as (G), the high shrinkage of the powdered glass on sintering leads to an unreliable final contour.

In (E) the shrinkage in sintering is accommodated by a sagging-in of the top surface of the solder glass section.

Narrow or irregular gaps as indicated in (F) and (H) are difficult to fill initially with solder glass, and suffer from subsequent shrinkage both in drying and firing.

With due consideration of seal geometry, devitrifying solder glasses have found many useful applications and we feel sure that many more will follow.

METAL DIFFUSION TECHNIQUES AND GLASS SEALING PROBLEMS IN THE ELECTRON TUBE INDUSTRY

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This paper deals with early techniques of chrome diffusion and the more recent method of chromizing of metals. Historical applications of the process as applied to certain glass sealing metals, its effect on the coefficient of thermal expansion and the interface between glass and metal, as well as proper seal geometry, are discussed. Pre-cleaning, oxide formation, glass application, seal types, and post removal of the oxide are explained along with accompanying subject pictures.

INTRODUCTION

Surface diffusion techniques applied to metals are not new processes. Carburizing methods were known even to primitive metallurgists. The diffusion of chromium into metals is, however, a much more modern technique, dating from about 1920, and the commercial application of chromizing processes is more recent still, probably beginning in Germany during World War II. Basically, the mechanism employed is one of a gas transfer from some chromium source to the work, with solid state diffusion at the work surface resulting in an alloy formation with true metallurgical bonding of the chromium to the base metal. Many minor variations are possible in the actual technique, but the gaseous transfer medium is almost always a halide, and the source of chromium is either flake, powdered or pelletized chromium or chromium compounds and mixtures. In some instances the work is supported in a finely divided pack containing chromium through which the halide gas permeates. Obviously, techniques which depend on solid state diffusion for alloy development will be high temperature processes. Chromizing is usually conducted at temperatures ranging from 760° - 1093°C.

All of the articles described in the present paper have been chromized in what is termed a "pack" chromizing process. That is, the work is embedded in a finely powdered mass containing chromium and an inert extender which prevents sintering together of the pack. An ammonium halide energizer is incorporated into the pack which manufactures the desired atmosphere "in situ", and the entire mass is enclosed within an hermetically sealed retort for furnace processing. Patents, either issued or applied for, cover the techniques of application and articles described herein.

HISTORICAL

Historically, application of chromized parts in the electron tube industry has been interesting. The first such parts processed were molybdenum leads, coated with chromium. The reason for doing this was chiefly an economic one, to effect the simple substitution of molybdenum for tungsten. By protecting molybdenum from oxidation during the sealing operation, it was hoped that this material might be substituted for tungsten and useful savings realized in the material cost. Assembly of experimental envelopes showed the technical feasibility of the operation and the reliability of the seals made using simple air sealing techniques.

This work was done some years ago, and at the time the glasses suitable for sealing to molybdenum were not at all common, were made in small quantity, and were quite costly. So costly, in fact, that they completely overshadowed any savings possible from the substitution of molybdenum for tungsten. Thus the situation arose wherein the glass was expensive because it was used in small quantity only; it was used in small quantity because molybdenum could not be easily glassed in air; and no one was interested in coated molybdenum because the necessary glass was so expensive!

In recent years a renewal of interest in molybdenum for tube purposes has occurred for reasons which are well known to all here. We have been gratified to find that a once abandoned technique is finding use again, and have been stimulated to extend the process to include other common sealing metals such as tungsten, Kovar, #4 alloy and the like.

The philosophy behind the coating of these materials has been to provide them with surfaces which could easily be converted to provide the tightly adherent chromium oxide that is so advantageous for glass sealing without altering the coefficients of expansion and creating a mismatch with the glass.

TECHNICAL DISCUSSION

There are three major physical considerations in the development of sound vacuum tight metal to glass seals. The first, and possibly major factor, is a proper match of the coefficient of thermal expansion of the metal portion to the glass. The second is the soundness of the joint, or interface, between the glass and the metal component. The third factor is seal geometry.

Control of the coefficient of expansion of glass sealing alloys is achieved by close control of alloy chemistry, and appropriate alloy-glass combinations have been worked out over a period of some years. Unfortunately, alloys having optimum expansion characteristics are sometimes difficult to seal because of poor surface properties which develop a weak glass to metal interface. It has long been recognized that chromium oxides form excellent bonds with glass. When a high chromium content exists in the metal to be sealed, oxide surfaces are readily obtained by controlled oxidation of the metal as a preparatory step. Thus, the chromium ferritic group of the 400 series of stainless steels can readily be treated to form oxide surfaces which are coherent and firmly attached to the base metal, and which also form excellent bonds with appropriate glasses.

Other common sealing alloys such as Kovar, which do not contain chromium but may be treated by the chromallizing process, are vastly more difficult to prepare in a manner that will produce the desired oxide on the surface. The result is a penalty paid either in unreliability of the seal formed, or high cost for elaborate and closely controlled preparatory steps.

With materials such as molybdenum and tungsten, some of the oxides formed are volatile, and sealing may have to be conducted under protected atmospheres, in sheaths or the like.

The heart of the chromallizing process described here is a surface alloying of the metal to be sealed with chromium. A thin layer is deposited. Thick layers, when oxidized to form the bonding surface, would diffuse sufficiently into the base metal to alter its chemistry and, hence, its expansion characteristics causing a mismatch with the glass. The high surface chromium content makes oxidation a routine and simple treatment, and permits even molybdenum and tungsten to be sealed readily in open air.

The strength of the seals developed is extremely high, and this permits the use of some unorthodox material combinations. Thus chromallized tungsten has been sealed directly to Pyrex.

PREPARATION OF CHROMALLIZED PARTS PRIOR TO SEALING

It has been found, so far, that parts prepared in this manner need no precleaning prior to oxidation unless they have been subjected to handling or surface contamination. Oils or greases from handling should be avoided. They may be removed by the use of standard degreasing agents such as trichlorethelene vapor, Diversey 909, or similar solvents by immersion for several minutes followed by a thorough flush in tap and distilled water with a possible final alcohol rinse to hasten drying. Contaminants which affect the surface are to be avoided. Strong acid baths may be required in order to remove the contaminants and may therefore, in turn, cause surface pitting leading to seal failure. Sealing conditions of certain alloys have been enhanced by fine sandblasting or tumbling of the sealing surface followed by careful clean up prior to undergoing chromallizing.

OXIDE FORMATION

In general, both pure metals and alloys require hydrogen clean up prior to oxidation. In the preparation of the metal before and during the addition of chromium, a careful schedule of hydrogen firing must be set up and maintained. This schedule of time and temperature varies in accordance to the metal under consideration.

Oxidation follows in the same manner with a variation in the schedule to suit sealing requirements. Errors made in the depth of oxide may be rectified prior to glass sealing by the use of standard techniques; of course, it must be

Figure I

CHROMALLIZED Kovar sealed to 7052 Glass showing tenacious Chromium oxide-Glass interface. The CHROMALLIZED coating provides additional protection for the Kovar during the oxidizing and sealing operations.

realized that the depth of chrome in the chromallized piece is of the order of .0005 - .001 and once this depth is affected by any reclamation process, poor sealing characteristics may result. Some photomicrographs have been prepared illustrating the nature of the seals obtained in Kovar and other metals. Figures 1 and 2 show cross sections of good and poor conditions.

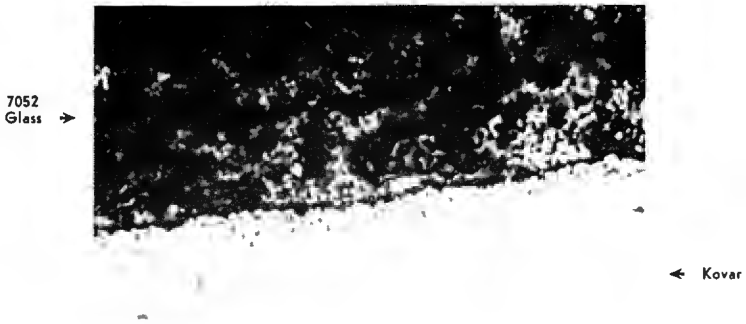

Figure 2
Un-CHROMALLIZED Kovar sealed to 7052 Glass shows intergranular attack on the unprotected Kovar. This attack may occur during the oxidizing and/or glass sealing operation.

Figure 3A
CHROMALLIZED and Oxidized Sylvania #4 Material, prebeaded and sealed to G-12 Glass.

GLASS APPLICATION

Sealing may take place as the parts are removed from oxidation process or they may be stored in dust and contaminant free containers for several days prior to sealing. The addition of glass frits and a subsequent firing at the proper temperature for both frit and metal may be carried out or the part may be directly sealed as required. As in the case of Sylvania #4 or similar alloys, the part may be inserted with or without preglassing. Figure 3- A & B shows the tenacity of oxide film in each case.

Figure 3B
CHROMALLIZED AND OXIDIZED SYLVANIA #4 MATERIAL SEALED DIRECTLY TO G-12 GLASS. The thin oxidized coating is extremely tenacious to both the glass and base metal.

Pre-beading is recommended in the use of tungsten or molybdenum. No additional oxidation should be attempted or should be necessary beyond that obtained previously. See figures 4 and 5.

Kovar or similar alloys prepared by this process have the unique chrome green oxide color. The technician need not be concerned as to whether or not the proper amount of oxide has been maintained during sealing. This, in itself, is a great step in the processing of glass to metal using this type of alloy as well as tungsten and molybdenum. The tube manufacturer will immediately recognize considerable savings in this respect, both in labor and materials.

ANNEALING

No change in annealing schedules are affected by this process. It has been noted in some instances that sealing conditions have been improved by this process.

Excess sealing temperatures have had little or no effect on the finished product. Interestingly, it has been found that only moderate flame annealing was necessary to reduce strains to the safe use point in the samples processed.

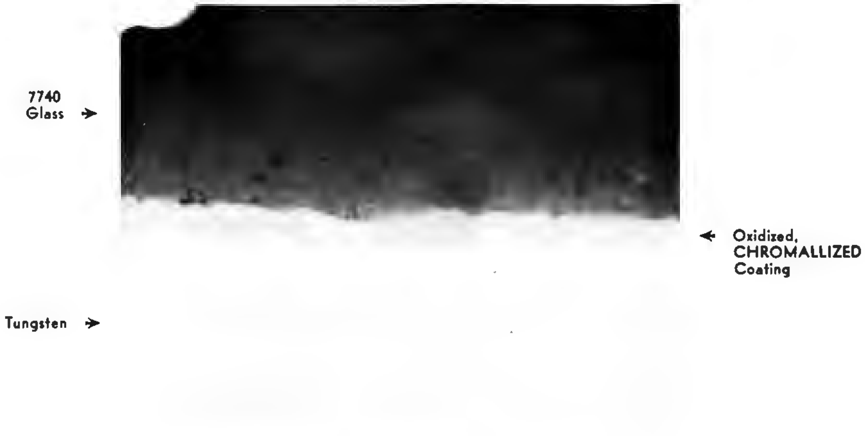

Figure 4
CHROMALLIZED Tungsten-Oxidized, then sealed to 774 Glass.

Figure 5
CHROMALLIZED Molybdenum-Oxidized, then sealed to 7052 Glass.

GLASS TO METAL VS. CERAMIC TO METAL ENVELOPES FOR ELECTRON TUBES

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I. INTRODUCTION

The purpose of this paper is to examine the factors affecting the selection of glass-to-metal or ceramic-to-metal envelopes for vacuum tubes. In device developments for both commercial and military uses, choice of the proper envelope construction for a particular device has become increasingly important because of the demand for better performance and longer life at lower cost.

Unfortunately, many workers in the field of electron tube construction are ardent advocates of either glass-to-metal or ceramic-to-metal envelopes without properly considering all the advantages and disadvantages of each. Often unknowingly, they may advocate designs which are much too costly, and from the standpoint of the user, provide greater performance capability than is required.

Before undertaking the geometric design of an electron tube, we must first decide whether the glass-to-metal or ceramic-to-metal envelope is best for the ultimate use of a particular device. This decision requires an evaluation of several factors which will be discussed later. However, let us first review some new developments in this field.

II. RECENT DEVELOPMENTS

Until recently ceramic-to-metal tubes were far superior to conventional glass tubes from the standpoint of high-temperature operation. Ordinary boro-silicate glass could not be baked out at temperatures above 450°C., while ceramic-to-metal combinations could be processed at 600°C. without a protective atmosphere.

This limitation for glass tubes is no longer valid. The use of alumino-silicate glasses and protective coatings for their sealing metals, molybdenum and tungsten, coupled with proper techniques for tube construction, is an alternative to be carefully considered. The commercial availability of alumino-silicate glasses no longer restricts their use to laboratory models.

Bell and Hillier[1] in 1954 first described the use of alumino-silicate glasses for electron tubes. They sealed molybdenum and tungsten to alumino-silicate glass in air and in inert atmospheres, but bake-out was accomplished only in a protective atmosphere to prevent oxidation of the metals. Today, the commercially available pack-chrome diffusion process adequately protects both molybdenum and tungsten during sealing to the alumino-silicates and allows high-temperature bake-out (600-700°C.) without the benefit of a protective atmosphere. The complete absence of a protective atmosphere should be stressed because it is of great importance for commercial large-scale production processes. Hees and Earley[2] have reported excellent results in the production of experimental vacuum devices using Corning type 1720 alumino-silicate glass and chromallized molybdenum to enable sealing and processing in air.

Because of the high working temperatures of the alumino-silicate glasses, the internal tube structure may be damaged in making the final seals. Solder glass sealing techniques now make it possible to produce reliable seals of intricate shapes without excessively high temperatures. This is particularly important, for example, when sealing-in a header gun structure to the rest of the tube, since high temperatures may be detrimental to the cathode. Solder glass also makes practical the resealing of tubes in case of seal failure.

The materials and techniques are therefore available for the production of alumino-silicate-glass tubes, although general acceptance has not as yet been received in the industry. Much inertia must still be overcome, because during the last ten years new production methods have been concerned mainly with ceramic-to-metal techniques.

Pyroceram has also received considerable attention recently, but its limited availability and limited glass working ability, with the exception of casting or pressing, gives it few if any advantages over the alumino-silicates at this time. However, if we could find a way to make a direct seal from Pyroceram to a metal suitable for lead purposes while the Pyroceram is still in glass form, it would then be possible to obtain an inexpensive construction for many types of special-purpose tubes capable of operating at high ambient temperatures.[3]

Ceramic-to-metal seals have not stood by idly during this period of high-temperature glass development. Of great interest is the use of beryllium oxide and the ability of this compound to be metallized and sealed to metals.[4] This material, although very costly and toxic when in powder form, has unusual properties. For example, its thermal conductivity is higher than that of molybdenum or tungsten at room temperature, although at elevated temperatures this benefit is reduced. For high-temperature applications, or where thermal shock may be a problem, the use of this ceramic merits serious consideration.

III. FACTORS TO BE CONSIDERED

So far, we have discussed some of the recent advances in glass-to-metal and ceramic-to-metal seals. Now let us examine the problems that a tube designer should consider before deciding what type of construction to specify.

Despite our intuitive feelings to the contrary, glass is a strong and reliable material. The glass envelope also allows visual inspection of the internal tube structure, which can be an invaluable aid in trouble shooting. Corrective action can often be taken without cutting open the tube envelope. Another advantage of glass-to-metal envelopes is that strains can be analyzed with a polariscope. Ceramic-to-metal envelopes, on the other hand, do not permit visual inspection of the electrodes, although X-ray analysis of such tubes can sometimes prove to be beneficial. Another obvious disadvantage of ceramic-to-metal tubes is the impossibility of measuring strains in seal areas. We must therefore place greater emphasis on the seal designs to minimize the chance of seal failures.

Resistance to shock and mechanical vibration are important for military applications. There is no doubt that for large structures, glass is often eliminated from consideration because of its inability to withstand severe mechanical shock. However, if the internal structure of the tube is designed correctly and the tube is properly shock mounted, glass can be as effective as a ceramic-to-metal envelope in resisting shock and vibration. The particular envelope material used has in most cases little effect on the operation of the device.

The thermal shock resistance of glass is relatively poor however, and for this reason many tube designers prefer to use ceramic-to-metal envelopes where the tubes must be capable of withstanding high ambient temperatures.

Resistance to radiation is another important consideration in certain applications, and one that is assuming increased importance. A considerable amount of information on radiation damage to tube materials is available for the various materials in use today.[5]

Studies by Spencer and Yamofsky[6] have shown that glass tubes generally crack or become gassy or discolor when exposed to thermal neutrons of the order of 10^{16} units of integrated thermal flux (n.v.t.). Apparently, boron in glass absorbs thermal neutrons, and this changes the properties and structure of the glass. This difficulty can be eliminated by manufacturing tubes from boron-free alumino-silicate glasses, such as Kimble type EE2, or Corning type 1715. Such tubes are able to withstand thermal neutrons of the order of 10^{16} n.v.t. without cracking, gassing or discoloring.

Ceramics, particularly aluminum oxide, when irradiated with approximately 3×10^{16} n.v.t., appear to suffer no damage. Metals commonly used for tube envelopes are not affected.[7]

We have already discussed the high-temperature bake-out capability of ceramic-to-metal and alumino-silicate tube envelopes without the benefit of a protective atmosphere. Tubes constructed from either material can be baked out at about 600°C. This is about the maximum temperature that tubes with such envelopes can be processed in air without gases from the atmosphere permeating through the envelope.

This permeation increases with temperature in both metals and glasses, and is also dependent on the pressure differential. For example, the rate of diffusion of hydrogen and helium through pyrex at elevated temperatures is directly proportional to the pressure, while the rate of diffusion of hydrogen through metals varies directly as the square root of pressure.[8] The rate of helium permeation through alumino-silicate glass is lower than with any other known commercial glass.[9] Certain ceramic-to-metal or alumino-silicate glass envelopes can, of course, be processed at higher temperatures if they are surrounded by a protective atmosphere or vacuum. As stated previously, however, such a restriction places limitations on volume production where cost is a factor.

The fact that refractory metals such as molybdenum and tungsten can be sealed to alumino-silicate glass causes some surprise for two reasons:

1) The metals oxidize rapidly at elevated temperatures.

2) It is difficult to weld internal tube components to these metals.

Oxidation can be prevented by the pack-chrome diffusion processes mentioned earlier. This chromallizing as it is called by its trade name, provides a protective chrome-rich surface which is then oxidized in wet hydrogen at about 1100°C. The oxidized chromium surface provides adequate oxygen resistance for direct flame sealing at 1200-1300°C. and also for extended high-temperature bake-out.

For certain applications the use of chromallized pins presents a problem because oxidized chromallized molybdenum or tungsten is reported to have a contact resistance about 50 times that of untreated molybdenum.[10] This would necessitate the cleaning of each pin after sealing, a prohibitively costly procedure for high-volume production. Welding the internal tube structure to the molybdenum pins is also difficult and costly. This problem can be solved by butt-welding nickel pins to both ends of a short section of chromallized molybdenum or tungsten pins; the internal tube welds are thus made to nickel and the contact to the socket or external circuit is also to nickel. Tests of pins made in this manner with either chromallized molybdenum or tungsten have shown them to be satisfactory.

In selecting the proper tube envelope, the relative costs of ceramic-to-metal and glass-to-metal tubes should not be overlooked. Generally, glass tubes can be produced at lower cost. The expense of forming and metallizing ceramics and high-temperature brazing of ceramic-to-metal assemblies adds much to the cost. Yet the fact that ceramics can be machined to exact dimensions provides a high degree of uniformity and dimensional rigidity, and also permits the use of simplified assembly techniques.

So far we have said little about the suitability of glass-to-metal or ceramic-to-metal seals in relation to the particular type of tubes to be made. For ordinary tubes, such as in home electronics equipment, soft glass is obviously adequate. Where high reliability is a requirement, high-temperature bake-out and resistance to radiation damage may be desired, but in most cases these requirements can be satisfied with present envelope materials. Alumino-silicate glasses and Pyroceram are also suitable for many such applications and should be less costly than ceramic-to-metal construction.

Now let us examine microwave and other special-purpose tubes. High power tubes usually employ ceramic-to-metal envelopes. Beryllium oxide in particular is useful in such applications because of its superior thermal properties and insulation resistance. Large structures which are usually characteristic of high-power tubes can best be accurately assembled with close-tolerance ceramic-to-metal seals. In the low power range, the alumino-silicates may be suitable and relatively inexpensive. The use of Pyroceram for operation at ambient temperatures above 350°C. will probably increase as soon as these materials become more available and improved techniques for their fabrication are developed.

IV. CONCLUSIONS

Ceramic-to-metal tube envelopes have found a worthy competitor for many applications in the alumino-silicate glasses and to a small extent in Pyroceram. One cannot generalize however, that one material is superior to another. In the interest of good engineering practice and of meeting design objectives at the lowest cost, we should examine all possibilities. Ten years of emphasis on ceramic-to-metal techniques should not give rise to short sightedness in capitalizing on new approaches and materials that take full advantage of well-established and lower-cost methods.

Sincere appreciation is expressed to Mr. Dan Lazare for critically reviewing this paper.

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TRAINING METHODS FOR GLASSBLOWERS

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The term "glassblower", as used here, is broken down into three categories, lampworker, latheworker and toolworker. Lampworking is generally considered to require the greatest manual dexterity, and consequently is considered the most skilled.

Training programs in the past have been designed primarily for lampworkers, and developed around the theme of improving manipulation, simultaneously imparting sufficient knowledge for the proper use of the skills, as they are required. Everyone agrees that this is a logical approach, but, one in which the value of each program hinges on the thoroughness of the training; that, learning to do one, or two orperations well, does not make one a glassblower.

As our ability to define has progressed over the last twenty years, training has become more formalized, and one could predict from observing the trend, that the competent glassblower will be accorded profession al status within the next twenty years, paralleling the situation in Europe. The professional glassblower will be one who has had at least two years of science, and science-related academic training, in a school above the high school level, plus perhaps 4000 hours actual work covering the various skills.

The history of this evolution to date in the South Jersey area starts prior to 1900, with the arrival from Europe of a number of Guild trained tank workers, and apparatus makers. Most of these were of German origin and were trained under a four year apprenticeship.

Since the level of scientific knowledge was comparatively meager at that time, little was required except an aptitude in manual skills. A viscosimeter, for instance was a piece of capillary with an enlargement at each end, and the viscosimeter constant for each tube was necessarily determined for each set of conditions. *Now,* we are able to construct a *Specific Constant* Viscosimeter in which we can control the accuracy of the constant to ± 0.1%, minimizing the kinetic energy correction in construction, and correcting for it from a theoretical curve, if a correction should become necessary.

The present mature generation of glassblowers has been trained by guild type workers, having served a four year apprenticeship in fundamentals, and then adding to skill and knowledge each according to his ability and opportunity. What was taught as fundamentals was left to the discretion of the teacher. Those who were fortunate enough to have specialists available, were instructed by several teachers, that is if the teachers were willing, because, remember, a type of Guild system was still in effect, and the secret know how of each member was jealously guarded. This was, in a manner of speaking, instruction though a natural method of selection, because the character of the apprentice was also being appraised.

One cannot deny the efficiency of this training, for, so far as we are aware, Ace Glass Inc. has trained more glassworkers who entered into business for themselves, than any other glassblowing organization in the U.S.A. Of these, nine are known to be established permanently, with a total estimated gross sales in the neighborhood of 3 million dollars a year. As you can see, it is hard to estimate the cost to us of training some twenty-two, one time competitors, and one can seriously question the wisdom of complete training for the individual by a company.

With the advent of unionization in the early 40's, Ace Glass Inc. (then being only 4-5 years old under this name) began a program of working out studies for apprentice lampworkers. Today the apprentice serves 3½ years or 7000 hours, whichever comes first. His manipulative training is divided as follows, more or less in the sequence listed:

TABLE 1

Operation	*Hours*	*Product Example*
1. Fire polishing; pulling points; round bottoming; and bending	200	Burrete Tips, Pipettes, Centrifuge, Tubes, Manameters
2. Solid seals; Shaping solids	300	Stirrers
3. "Stick" seals	1000	Stopcocks, Burettes
4. Simple small seals	1000	Simple adaptors Gas manifolds
5. Larg blow seals	1500	Small neck flasks, Gas sampling tubes
6. Large to small seals 7. Simple ring seals	100	Traps
8. Harder ring seals	1000	Condensers—all types
9. Use of pick—(advanced)	300	Vigreaux Columns, Other simple columns
10. Large ring seals (more detail)	300	Distilling Heads Simple types
11. Volumetric work (increased detail)	300	Receivers—Distilling and Moisture test
12. Advanced work, and/or Concentration on Weaknesses	1000	Misc. items—Specials
Total	7000	

This represents the average worker's needs; a more gifted person might accomplish the same result in 4000 hours, which we would regard as the minimum time for professional status under any training program.

With the arrival of World War II, the scarcity of glassblowers became evident; and after the shooting stopped, the Veterans Administration approved glassblowing as a trade which they would subsidize. This required a course approved by the New Jersey Dept. of Education, and encompassed the teaching of manipulative techniques plus selected lessons in physics, chemistry, mathematics and blue print reading. The academic material was taught by Mr. C. I. Kramme of our organization, who has a masters degree in education. His courses were given three nights per week.

In 1959 Salem County N. J. established a Vocational-Technical Institute which offers two year diploma courses to high school graduates at a nominal tuition ($50.00 per year to residents and $150.00 per year to non-residents of the County).

The courses are classified as public education, and come under the supervision of the N. J. Dept. of Education. Standard college entrance requirements are necessary for admission.

The Glassblowing Course, offered at the school, is believed to be the first one of its caliber in the U.S.A. Using the teaching outline of Mr. Kramme as a starting point, the academic material was enlarged by subject and upgraded to junior college level, an advisory committee, composed of representatives from 6 manufacturing companies and 3 education members, specified the requirements for the major subject, glassblowing. This advisory committee now has official status in the state, its recommendations become part of the school law.

The curriculum covers the following subjects:

First Year (18 weeks)	*Hours Per Week*
Scientific Glassblowing	15
Industrial Chemistry	4
Mathematics	4
Blueprint Reading and Drawing	3
Technical English	4
Second Year (18 weeks)	
Scientific Glassblowing	15
Physics	6
Mathematics	4
Technical English and Report Writing	2
Machine Shop	3

The total of glassblowing hours is 540, which may be applied against the 7000 required for apprenticeship in those plants which are committed to the union guild system.

I would venture the opinion that the graduates of the school are adequately trained to make simple apparatus, and most repairs, providing the time factor is not critical.

The success of this course to date has been better than expected, and evening courses are in the planning stage. Two basic courses are contemplated, the first an elementary one designed for chemists, laboratory technicians, science teachers, and similar personnel. The second course is intended to help the glassworker who finds himself in a rut, making perhaps one or two items day in and day out, and who wishes to improve his lot. In this course the student's ability, and knowledge already gained, will be ascertained, and a course then will be individually plotted for him to round out his education. The project method most likely will be used, so that progress can be realized in definite steps. Apprentices may also enroll in this type course to shorten apprentice time in years.

You will note first of all that the public education program is designed to combine the best features of the guild method and the academic method, giving well rounded basic training to small groups where group training can be advantageous, and individual training when specialized and difficult techniques of manipulation are taught.

Secondly, the training in primary fundamentals is standardized, so that any employer, upon hiring such a person, knows that his training up to that point is satisfactory.

Third, that he has the proper background for advanced training, a background which is not only accepted, but endorsed, by large manufacturing groups, and the job opportunities of the graduate are thereby widened.

Fourth, the foundation is formed upon which a professional glassblowing status can be built for scientific apparatus workers.

Fifth, it presents the opportunity for advancement to those who feel the need for more professional training, and who otherwise might not have the opportunity.

Further information such as some teaching outlines, drawings of items made during the first year of the course and some teaching aids, will be available during the panel discussion this afternoon.

VACUUM FORMING OF GLASS

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INTRODUCTION

Vacuum forming of glass is a relative newcomer to the venerable field of glass and glass technology. While glass itself dates back to earliest antiquity and glass blowing to at least 20 centuries, the first crude vacuum reforming of glass started only about 50 years ago.

The real impetus for vacuum formed glass was derived from the need for tapered glass tubing of accurate internal dimensions which could reproduce its calibrated I.D. dimensions from tube to tube. As a manufacturer of flowmeter tubes, the Fischer and Porter Co. became involved in the manufacture of precision bore vacuum shrunk tubes (Fig. 1 & 2) for its flowmeters and by extension to an increasing array of plain and fancy shapes.

PROCEDURE

The vacuum forming of glass is simple in principle. A raw glass tube which is bottomed off or stoppered at one end is evacuated by means of a pump. The temperature of the glass is increased to the region between the upper annealing temperature and softening point by means of torches, an oven, electrical resistor, secondary radiator or other means.

Atmospheric pressure causes the tube to collapse around the mandrel starting at the closed end where the heat has been first applied and proceeding along the length until the desired portion has been shrunk. At this point, the heating is discontinued and the glass and mandrel permitted to cool. The latter which has a greater thermal expansivity is removed and the vacuum reformed tube is ready. This can be simplified even further by evacuating the tube and sealing with the mandrel inside. The encapsulated mandrel is then inserted in an oven without any vacuum connection and reformed.

However, the consistent large scale manufacture of high quality vacuum formed tubing is a demanding task which calls for an extensive application of glass technology and ingenuity. Some of the elements involved will be indicated.

GLASS

Precision starts with the raw glass tubing. Raw glass should be selected for the maximum freedom from defects such as air lines, striae, crystallites, knots, stones, grooving, bow, etc. The glass should be clean, dry, and have sharp edges removed to avoid scratching the mandrel. In reforming a glass, appropriate provisions have to be made for the specific glass composition and its physical and chemical properties. Thus a neutral or oxidizing atmosphere might be used for a glass rich in PbO to avoid reduction, a reducing environment with a specific aluminosilicate glass to avoid reboil, and a sodium perborate solution treatment with a particular borosilicate glass to inhibit devitrification.

Successful vacuum forming has been done at the Fischer and Porter Co. in a large variety of glass sizes and types. These include fine capillary glass having

Figure I
Vacuum forming of flowmeter tube.

a precision bore as small as .002 inch and heavy glass almost up to a foot in diameter. Very heavy glass wall thicknesses up to two and three times the thickness of commercially drawn tubing have been made by lamination reforming. Tolerances on these glasses run from a few thousandths on the large size glass to .0002″ in smaller sizes. In special lots small bores have been made with a precision of ± 25 millionths of an inch.

With respect to glass types most of the commercial glasses as well as some optical ones have been successfully vacuum reformed. These include soda line, borosilicate, soda and potash lead, aluminosilicate, phosphate glass, barium glass, Vycor and fused silica glass.

Figure 2

Section of vacuum reformed flowmeter tube with guide beads and float.

MANDRELS

Mandrel material may be selected from a large variety of metals and alloys. The thermal expansivity of the mandrel must be greater than that of the glass to permit removal of the latter upon cooling and it must have good high temperature corrosion resistance to withstand the temperatures required for the particular glass.

Mandrels may be specially shaped to produce various geometric cross sections, beads, fats, flutes, stops, threads, or markings in the glass. They may be split or joined to produce complex shapes.

DEFECTS

Defects in reformed glass can cause a very high rejection rate unless very careful control is exercised. Cold crack can be occasioned by the reformed glass contacting a mandrel which has not been sufficiently preheated. Sealing can result from excess heat in the mandrel. Devitrification and reduction in certain glasses will occur in spite of favorable chemical environment under certain time-temperature schedules. Dirt requires thorough and constant housekeeping. Excessive temperatures will cause "burns" in the glass.

ANNEALING

Glass which has been vacuum formed generally has an excessive amount of strain. In heavy walled glass this may be sufficient to cause spontaneous breakage if it is not relieved within the same day of fabrication.

Annealing can generally be done best in batch ovens that are carefully controlled for uniformity of temperature. It can also be done in continuous lehrs. A partial anneal can be imparted with a follow up annealer during the reforming operation.

The annealing schedule used is controlled by the type of glass and the thickness of the ware. In addition to relieving the "permanent" strain due to temperature gradients after cooling from the fabrication operation, annealing affects the chemical and physical properties of the glass in a very slight but measureable fashion. While this is not significant for ordinary glassware, for precision glassware it can be of vital importance.

Thus a change in ID of a few ten thousandths of an inch as a result of an annealing cycle can cause the tubing to be thrown out of its tolerance and reduced to scrap. Conversely, by the use of controlled fine annealing, out of tolerance tubing can sometimes be restored to its proper size.

FURTHER OPERATIONS

After reforming, additional operations are performed like cutting, grinding, graduating, etc. Operations like metallizing may be performed simultaneously with a vacuum rundown.

Fire polishing is used to protect the ends of the tubes. To impart greater strength to the tube, a selective tempering operation may be used. As more sophisticated designs and tighter tolerances are required, vacuum reforming will find an increasing role as a means of making precision glass.

THE USE OF DEVITRIFIABLE SOLDER GLASS IN EXPERIMENTAL VACUUM DEVICES

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Bayside, N. Y.

One of the most intriguing and challenging contributions of recent years to glass working is that of devitrifiable solder glasses. These are finely divided frits which, upon proper heat treatment, melt, flow and cure into glass-bonded ceramic bodies. They can be used to cement a number of materials together with less stringent thermal expansion matches than glass-to-metal seals.

The fritting technique is a simple one: a slurry is suspended in nitrocellulose lacquer and applied to parts by flowing, dipping, or brushing; the coat is then dried and the parts are fired together. The advantages of the technique become immediately evident; the curing temperature of the frit is far below the deformation temperature of the glass, so control of starting geometry is assured. Close-tolerance work is simplified, and shapes impossible to make by all but the most experienced glassblower are readily achieved.

Most of the work at the General Telephone & Electronics Laboratories at Bayside has been with Corning Pyroceram, #95 and #45.* Cement #95 matches soft glasses and their sealing metals. Cement #45 matches the alumino-silicate glasses, molybdenum and tungsten. Both cements have a curing range, but almost all of the work done at these laboratories has been within rather narrow ranges of temperatures for each frit. We have heat treated cement #95 at 440°C. for one hour and at 470° for half an hour. Cement #45 has been cured at 750° for 60 minutes and at 760° for 20 to 30 minutes.

We have used two types of furnaces for the curing operation. The first is a standard non-circulating top loading floor model shown in Figure 1. The second is a vertical wound serrated quartz glass tube contained in a quartz glass holder. An example of this type is illustrated in Figure 2. This type of furnace is used for tubular seals and permits zone heating. For temperatures below 500°, the windings are nichrome wire; for temperatures above 500° a platinum winding is used.

The application of fritting techniques in our laboratories has been almost entirely to low-power microwave tubes. Many nearly insurmountable problems of construction have been solved by the use of these seals.

To illustrate the usefulness of these techniques, we have chosen several devices that exemplify the advantages to be gained by this method as compared with conventional flame sealing. The first is a velocity-sorting detector, Figure 3. This tube consists of an electron source, a slow-wave structure (helix), an electron-optical velocity detection system, and finally a collector. The problem here was to seal the electron source and input coax line at one end of the tube and the detector, collector, and output coax at the other end. This problem was further complicated by the fact that the gun, helix, and detector do not share a common mount but are isolated from one another. Obviously, the problem of alignment between gun, helix, and detector is critical. All glass parts in this tube are

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*Corning Glass Works, Corning, New York

Figure I

fabricated from soft glass, and cement #95 is used for the seals. The electron gun end is fritted into place, and the other parts placed on a line-up mandrel which passed through the detector, the helix, and protrudes into the gun to within $\frac{1}{16}''$ of the cathode. The order of assembly from then on is the detector system, the two coaxes, and finally the collector after the line-up mandrel is removed.

Three seals are made one at a time at the detector end of the tube. The first seal at the detector end is therefore heated to 440° three times.

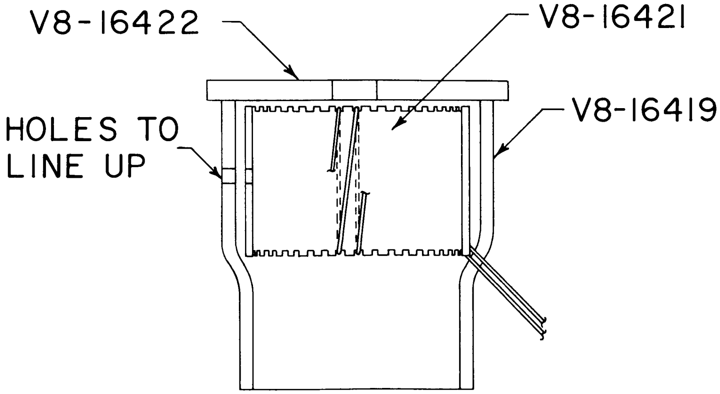

Figure 2

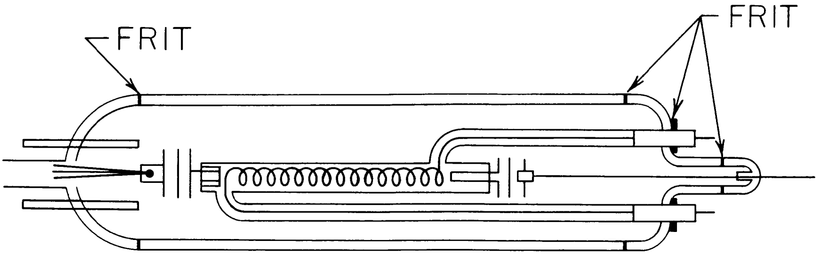

Figure 3

The second illustration of the fritting technique in soft glass is a rather special device that requires an electron optical system constructed of extremely thin metal parts. In order to meet this requirement, the entire electron optical system is made from glass parts coated with gold. The system consists of an electron drift tube, two flat anodes with 0.008″ apertures, and a third anode with a 0.030″ aperture. These apertures are spaced 0.015″ to 0.030″ apart; the structure is illustrated in Figure 4. Again absolute alignment is essential. The alignment is

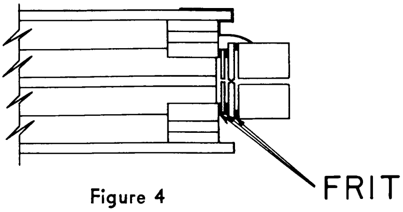

Figure 4

accomplished by using a jig and mandrel made from Sylvania #4 alloy, glass shim spacers, and connecting supports of frit. After curing each set of supports in assembly, the spacers are removed and fire-on silver painted from the individual aperture disks down the frit posts so that electrical connections to the apertures can be brought through the wall of the tube. At each step of fritting and silvering, the assembly is fired for one hour at 440°. There are eight separate firings of this assembly. The first frit applied is cycled and held at 440° for a minimum of eight hours.

The optical assembly is supported in a precision bore envelope by two spacer disks which fit over each end of the drift tube. The spacer disk at the optical end is fastened in place with a fillet of frit, the other disk left floating. The silver paint connections to the apertures are continued over this fillet and across the open end of the envelope.

The tube is closed by fritting the collector cap directly over the silver. Thus electrical connections can be brought out through the wall of the tube without the use of wires or conducting frit.

Efforts have also been directed toward the use of Pyroceram #45 with the alumino-silicate glasses, molybdenum and tungsten. Initial work with these materials was directed toward determining the effect of time, temperature, and atmospheres on sealing quality. The test vehicles were ½″ diameter glass tubings and 0.060″ diameter rods. Curing was carried out between 750° and 800° for from 20 to 60 minutes in the platinum-wound furnace. Carbon dioxide, argon, and forming gas were used as atmospheres. One conclusion drawn from these experiments is that water vapor accelerates curing time, aids frit flow, and assures vacuum tightness as shown by the fact that, when the flush gases were put through a drying train, the seals leaked.

The problem then was to introduce moisture into a seal area having components that could stand no moisture: tungsten, or molybdenum. Several methods were investigated in an attempt to protect the metals by coatings that would not oxidize or that could at least protect against excessive oxidation. Electroplating various materials on the rods was tried, but none proved to be reliable.

Chromallized* rods were obtained, and satisfactory seals with this material were made in water-saturated air; they did however, show molybdenum oxide break-through after three cycles to 600°.

Several chromallized rods were then oxidized in wet hydrogen at 1100°, and again seals made in water-saturated air. These were leak tight and showed no molybdenum oxide break-through after six cycles to 600°.

It must be pointed out that, with the oxidized chromallized rods and water-saturated air, a rigid heat schedule could be established. The frit melted at 675°, flow was observed at 690° and curing was carried out at 760°.

An alumino-silicate precision-bore waveguide was made for operation in a Dewar flask. Frit seals through the inner and outer wall Figure 5, were made without distortion of the waveguide. The outer wall was provided with a tooled bellows to compensate for thermal stresses set up during operation at liquid nitrogen temperatures.

There is a time-temperature relationship in the curing of 45 and 95 frits. It is one of minimum time and maximum temperature neither of which have

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*Obtained from Chromalloy Corporation, West Nyack, New York

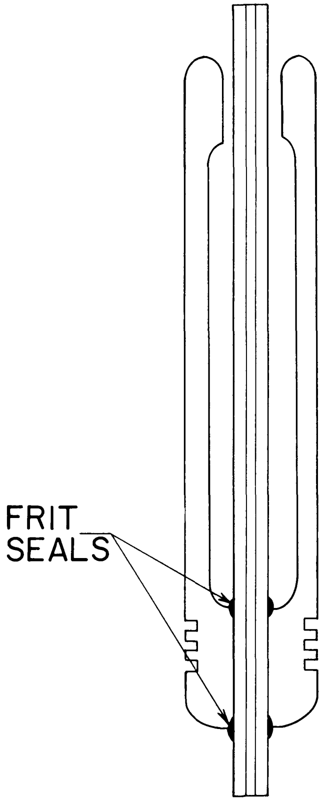

Figure 5

been fully explored. Too low a temperature or too little time effect a partial cure leaving an expansion mismatch between components and the cements. Too high a temperature and too long a time over cure these cements leaving them porous.

These are but a few of the many experimental structures we have made at Bayside using a fritting technique. They can only point the way to more new designs in glass and glass-metal experimental devices. The drawback of curing time is of less concern in the laboratory than of not being able to do the impossible. The techniques described are not meant to compete with production methods, but the basic principle could be adapted to production in some cases.

A SOLDER GLASS SEALED VACUUM ENVELOPE TO OPERATE AT 500°C. AMBIENT TEMPERATURE

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PART ONE
SELECTION & SEALING OF COMPONENTS

Introduction

In the last few years we have seen considerable activity in the field of high temperature components. Part of this effort has been a Signal Corps Contract* for the evaluation of Corning Glass Works Pyroceram No. 9606 as an envelope material which could serve in the same application where ceramics are used.

Pyroceram is essentially a material that has been converted into a crystalline ceramic from its original glassy state by the use of heat treatment. Nucleating agents are included in the glass batch. The desired shapes are formed and annealed by standard methods. Subsequently the glass is reheated and crystallites are formed which act as centers for crystal growth as the heat treatment continues. The resultant material is a uniform, opaque ceramic of the same shape as the original glass article. Dimensional changes during heat treatment are less than 1%, minimizing finishing of precision contours after conversion to ceramic form[1]. Consequently it is possible to produce articles with Pyroceram No. 9606 to very close dimensional tolerances, especially since it can be ground in the glassy stage. A commercial advantage of Pyroceram No. 9606 over ordinary ceramics is the fact that it can be fabricated into various shapes by well known mass production methods such as casting, blowing, or pressing. Since the ceraming process changes the material from a glass to a ceramic, conventional glass sealing techniques employing flame working could not be used to seal two parts of Pyroceram No. 9606 together. Other methods of joining had to be found and developed.

The Pyroceram No. 9606 selected for this work has a coefficient of linear expansion of $57 \times 10^{-7}/°C.$ (from 0-300°C.) which is lower than that of high density alumina and most other ceramics.

The thermal expansion graph of No. 9606 Pyroceram shows also the expansion of tungsten, molybdenum and Kovar (Figure 1). From these three metals it was decided to eliminate Kovar because of mismatch in thermal expansion. It was believed best results could be expected with tungsten, but it was decided to explore both molybdenum and tungsten of .020″ to .030″ diameter. The greatest mismatch between the metals and Pyroceram No. 9606 is at 180°C.; however at temperatures above 500°C. tungsten is the better match.

Treatment & Joining of Components

The envelope is designed in the form of a dish with narrow flanges which are provided with grooves. The grooves receive the lead wires and exhaust tubulation (Figure 2).

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*Contract No. DA-039-SC-75076, U.S. Army Signal R & D Laboratory, General Tubes Branch, Fort Monmouth, N. J.

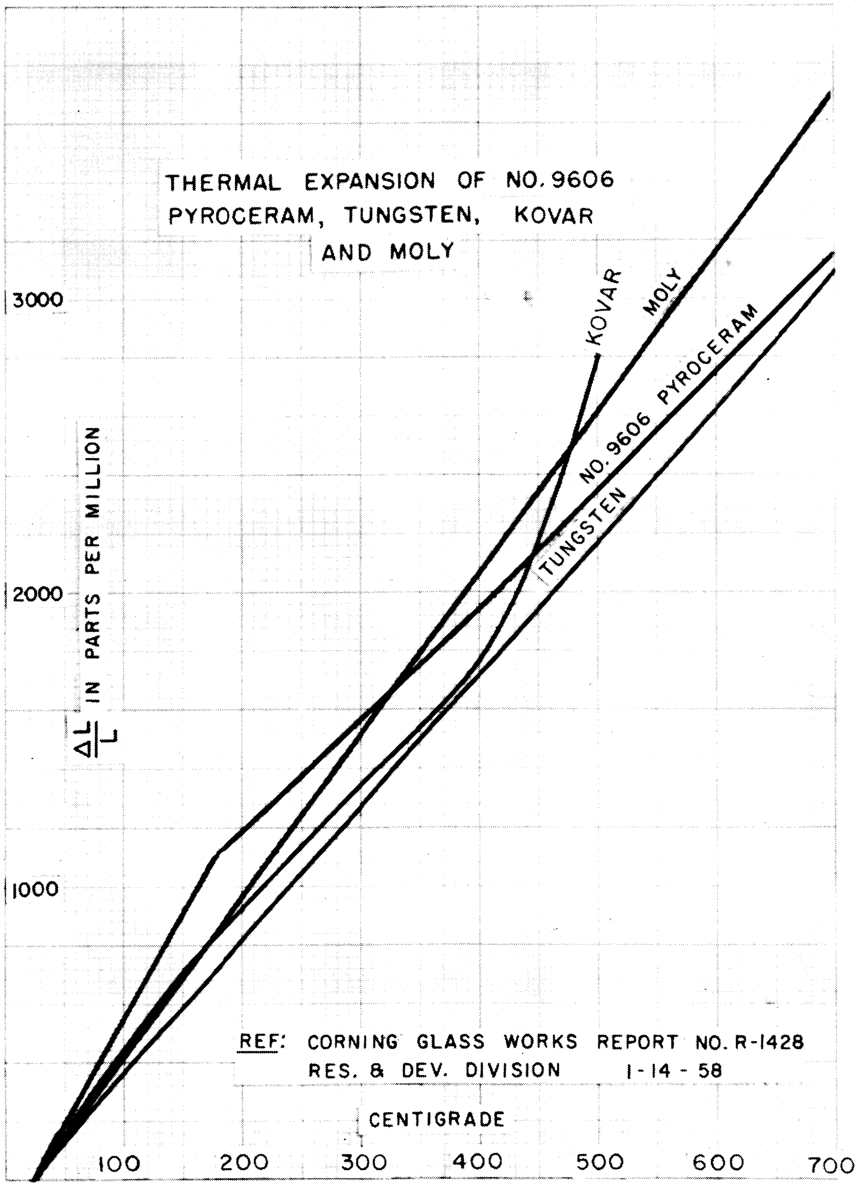


Figure 1

Much consideration was given to the selection of proper metals for high temperature lead wires. This subject will be covered in its entirety in the second part of this paper.

Pyroceram No. 9606 tubing was found unsuitable for exhaust tabulation. When heated sufficiently difficulty was experienced in tipoff because of a very short

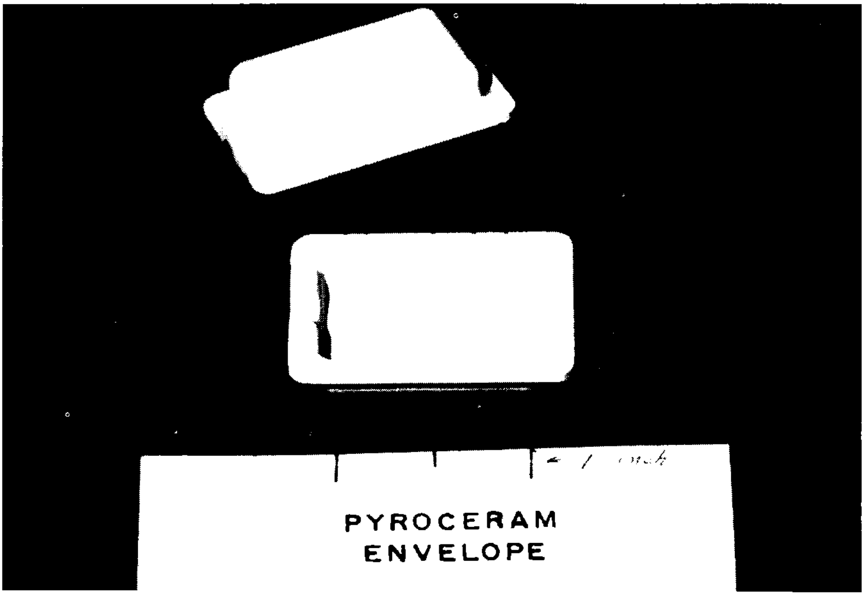


Figure 2

plastic range. A suitable glass namely Corning Code 1720 Alumino Silicate was chosen. Direct insertion of this glass tubing into the envelope developed strain cracks in the tubing. Therefore a two piece exhaust tubulation was provided. A 1¾" long piece of No. 1720 tubing is sealed manually with a gas oxygen burner to a short piece of Pyroceram No. 9606 tubing. Care must be taken that most of the heat is applied to the glass tubing; overheating of the Pyroceram tubing will cause brittleness and must be avoided. The Pyroceram section of this exhaust tubulation assembly is then coated with a thin layer of Pyroceram cement No. 45, dried, and pre-glazed.

No. 1720 tubing has proven to be the most suitable material; it has extremely low permeability and low gas release properties. Experimental tipping has been performed on evacuated vessels resulting in short, strain-free tips and has been found satisfactory.

In assembling the Pyroceram envelope with its exhaust tubulation the two piece lead wires were chosen with the inner section of tungsten and the outer section of low carbon nickel. Attention must be given to the location of the weld knot. Placing the weld knot inside the seal area was found unadvisable due to its larger diameter. The final arrangement locates the weld knot just outside the flange with the tungsten penetrating the entire seal area. Beading of the lead wire with solder glass must cover not only the tungsten part of the lead wire but also the weld knot (Figure 3).

Two types of solder glasses were studied and tested for sealing the envelopes, namely thermoplastic[2] (vitreous) and thermosetting (crystallizing) solder glass. After many tests it was decided that the thermosetting solder glasses held more promise for successful seals with Pyroceram No. 9606. Various compositions were supplied by Corning Glass Works with the end result of solder glass Lot 703-3

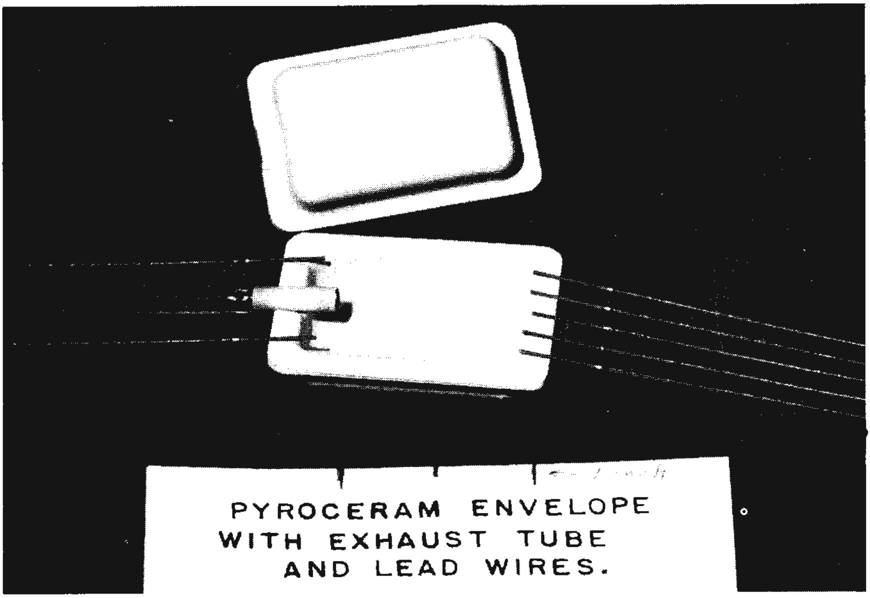


Figure 3

and 703-4 providing the best results. This solder glass is now sold by Corning Glass Works as Pyroceram brand cement No. 45 or also as solder glass Corning Code 7574[3]. It is a finely powdered glass of a special composition and the degree of crystallization obtained is a direct function of temperature and time. It can be applied to the sealing areas by dipping, pressure flow, brushing or by use of any other desirable method. The uncured glass after complete evaporation of the binder is chalky and does not render a satisfactory seal. However when the glass is fired according to schedules a change in material occurs.

The glass develops first a vitreous phase and then on further continuation of the firing cycle a partially crystalline structure which results in a devitrified glass seal which may be much stronger and harder than the original glass. The thermal expansion for No. 7574 solder glass is 42 x 10^{-7} from 25°C. to 650°C. after devitrification at 750°C. for one hour.

Thermoplastic solder glasses usually have a deformation point considerably lower than the sealing temperature; consequently bakeout temperatures are limited to lower temperatures. On the other hand, devices sealed with thermosetting solder glass can be baked out much closer to the original sealing temperature. The sealing temperature can even be exceeded for short time bakeout cycles without any apparent damage to the seals.

A binder that would hold the solder glass particles in place on the sealing edge until firing had to be selected. Binders must have at least the three following qualifications:

A. Must completely evaporate before the glass becomes soft.
B. Must not leave any carbon or other residue.
C. Must have good flowing characteristics and adhere well to parent glass to permit some handling without falling off before firing.

Twelve different binders were tested; and for the final seals Corning Glass Works recommended nitrocellulose in amyl acetate binder was adopted.

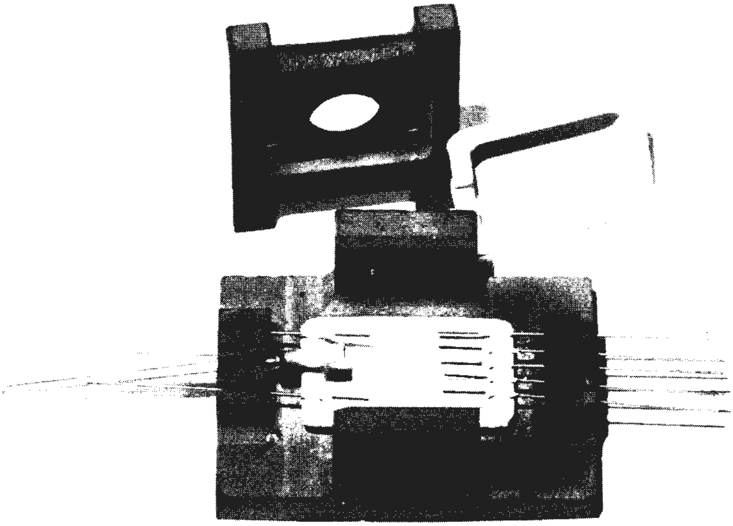
The final sealing schedule arrived at by our laboratories after various studies and modification is as follows: Inspect envelopes with microscope for pin holes, hairline cracks or enclosed impurities. Test flanges for planar alignment. Clean envelopes with amyl acetate by wiping with clean cloth and dry.

Mix No. 7574 solder glass with the nitrocellulose vehicle to a viscosity similar to molasses. Best results are achieved if the composition is rolled on a ball mill for several hours, possibly overnight. Apply to flanges with a glass dip stick, approximately 20 mils thick. Dry under infrared lamp for 30 minutes.

Pre-glaze envelopes in an air atmosphere at 610°C. to 620°C. for 5 min. Start heating cycle at room temperature and maintain a heating and cooling rate of about 4°C. per min. The small checks which may appear in the solder glass layer after pre-glazing are due to expansion differentials and are not detrimental. The pre-glazed parts should have a clear glassy appearance. A horizontal lathe is employed to apply the solder glass to the exhaust tubulation and lead wires. The parts are slowly rotated in the lathe and the solder glass paste is applied with a glass rod. Beading layers on lead wires should be about .010″ thick. For the exhaust tubulation the thickness of the solder glass applied depends on the diameter of the exhaust tubulation and envelope opening. An application of about .020″ was used with good results.

Exhaust tubulation and lead wires are then dried and preglazed under the same schedules as the envelopes.

For sealing, the components are placed in a sealing jig to hold lead wires, exhaust tubulation and the two envelope halves in proper relationship to one another (Figure 4). The cover plate is loaded with a metal weight of 200 grams,



SEALING FIXTURE WITH
ENVELOPE EXHAUST TUBE
AND LEAD WIRES.

Figure 4

making the total weight onto the envelope 219.5 grams. The sealing fixture is then placed in a stainless steel sand sealed box. The box is transferred to a furnace with the inlet of the box connected to a nitrogen line. The box measures approximately 7″ x 7″ x 7″. A flow meter shows the correct amount of nitrogen to be used for sealing. Two cubic feet per hour of pure line nitrogen for this size box yielded the best results. (Figures 5 and 6)

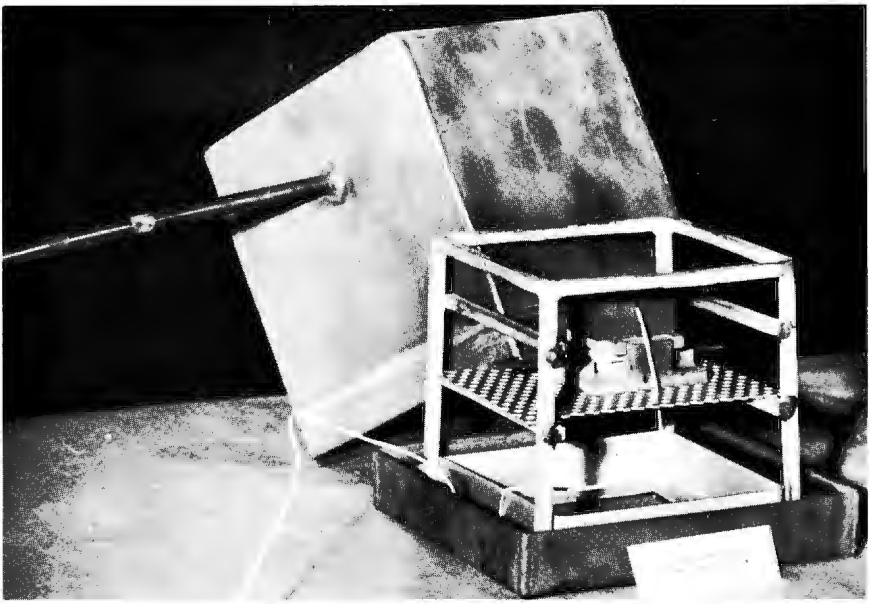


Figure 5

Sealing rates were held at 3°C. per min. for both heating and cooling. Actual sealing time was 60 minutes and the temperature 720°C. After cooling the tubes were removed from the sealing fixture, examined for defects and tested for vacuum tightness in a helium leak detector.

After vacuum testing the short exhaust tubulation was extended and a larger section of No. 1720 glass tubing sealed onto it. In this larger section were inserted two Kemet barium getters. The larger tubing was then constricted again and another section of small exhaust tubulation sealed to it.

The assembly was then inserted into an exhaust station or trolley and baked out at 750°C. for 20 min. After bakeout the assembly was tipped off and one getter flashed.

In the final finished assembly the getter supported by mica can be seen (Figure 7). The distance between getter and tube envelope of 2″ is necessary in order to heat the envelope to 750°C. while maintaining the getter enclosure at low temperature.

Test on Final Assemblies

Fourteen final assemblies were immersed for two minutes into acetone from 23°C. to –78°C.; hereafter from 0°C. water to 100°C. water to 0°C. for 15 seconds. No failures were detected when they were tested for vacuum after 72 hours.

Figure 6

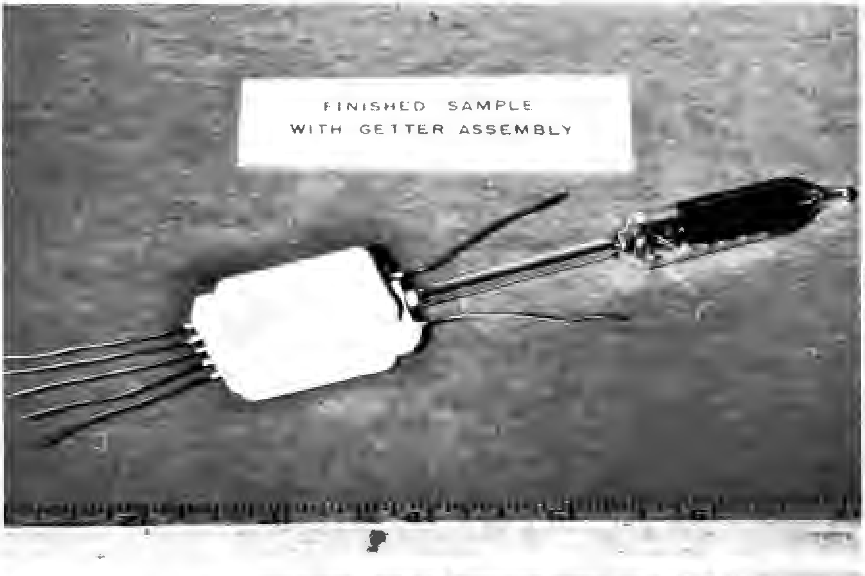


Figure 7

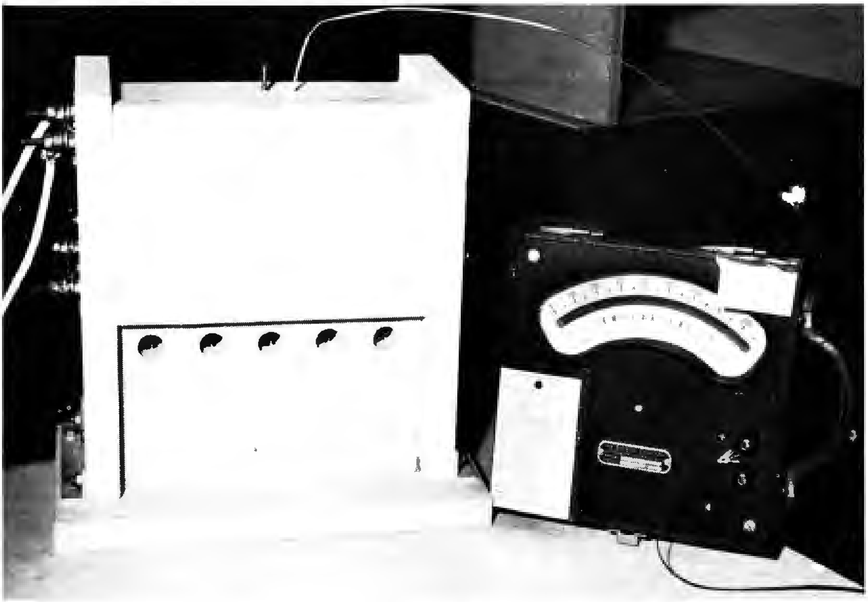


Figure 8

Thirteen final assemblies were heated during exhaust from 23°C. to 750°C. at an average rate of 40°C. per minute and cooled from 750°C. to 200°C. at an average rate of 20°C. per minute, without failures.

Ten final assemblies were tested according to Mil Std. 202, Method 106 (10 days humidity cycling plus freezing). Vibration was omitted and the specimens were examined for leakage and appearance after the 10 day test. Nine specimens passed this test without loss of vacuum or change of getter deposit; one specimen failed and developed a minute leak.

500°C. LIFE TEST—Five final assemblies were placed in a specially constructed oven which was adjusted for continuous exposure of the specimen at 500°C. in air (Figure 8). Every week the assemblies were examined and in the 500°C. test two failures were noted. One tube failed after 1409 hours of continued exposure; the other specimen failed after 1416 hours. The time accumulation for the other specimens ranged from 1508 hours to 1584 hours. Examination of the two failures showed oxygen present at sparking (pink glow) and the getter deposit had turned dark brown. The reason for failure was oxidation of the tungsten leads. With a time accumulation of over 1500 hours of exposure to 500°C. in air the test was discontinued. It was felt that the goal of exposure to 500°C. in air for a time of 1000 hours had been reached and exceeded.

400°C. LIFE TEST—Five final assemblies were placed in a specially constructed oven which was adjusted for continuous exposure of the specimen at 400°C. in air. Again every week the assemblies were examined for appearance, getter deposit, and then checked with the high frequency spark coil. After an average exposure time of 5600 hours all five assemblies were found satisfactory.

Related Experiments

Other thermosetting solder glasses, such as Pyroceram cements No. 89 expansion range 80-90 x 10^{-7}/°C. and No. 95 expansion range 90-110 x 10^{-7}/°C. have been used to seal large vacuum envelopes such as T.V. and radar tubes.

Thermoplastic solder glasses such as Corning Code No. 7570 with an expansion range of 90-95 x 10^{-7}/°C. have been used to seal matchbox tubes[4], using Corning Code 0120 glass as envelope material. Other thermoplastic solder glasses include Corning Codes No. 1826 expansion range 50-55 x 10^{-7}/°C., No. 8363 expansion range 105-110 x 10^{-7}/°C. and No. 9776 expansion range 130-140 x 10^{-7}/°C.

Kimble's electrically conductive solder glass "CC-10" has been used with 0120 glass for special devices and will receive continued attention in our laboratories.

We have been using powder glasses and solder glasses for some time to produce vacuum-tight devices. The combinations may include glass to glass, glass to metal, glass to ceramic, glass to mica to metal and glass to metal to ceramic. Large quantities of tubes have been produced using the powder glass techniques in sealing metals, ceramics and glass[5].

Solder glass sealing at various low, medium and high temperatures for vacuum devices may offer many advantages and some, as yet, unexplored possibilities. One of the principal advantages is the fact that seals can be made at substantial lower temperatures than the conventional flame-sealing techniques[6]. Another is the clean or protective atmospheres than can be used to minimize contamination of components and the prevention of oxidation.

Experimental seals were made in our laboratory using Corning Code 1723 Alumino-Silicate glass envelopes and various solder glasses with promising results. Experiments of similar nature have been carried out by other companies in similar fields[7]. The special properties of No. 1723 glass should offer many advantages in tube design over soft and borosilicate glasses and will receive continued attention as a high temperature envelope material in our development work. The limiting factor for bakeout of No. 1723 Alumino Silicate (and similar glasses) is in most cases the strain point, 665°C. A higher bakeout may be desirable and may even reach the annealing point, 709°C. In this special instance care must be taken to control the bakeout cycle in such a manner so as to prevent any deformation and strain.

Conclusions

For the operation of vacuum tubes at high ambient temperatures Pyroceram No. 9606 is a satisfactory material. Due to its comparatively low coefficient of expansion and mechanical strength it can sustain large temperature gradients and exhibits good thermal shock properties. The permeability to most gases at elevated temperatures is superior to many glasses and equal to the high purity aluminum oxide ceramics. Electrical characteristics are good for most applications. Volume resistance is less at elevated temperatures than alumina ceramics. The mechanical properties of the material are sufficient for most applications in the tube field.

Direct flame seals from Pyroceram No. 9606 tubing to No. 1720 alumino silicate glass and Corning Code glass 7720 were fabricated experimentally for the system to test the permeability of Pyroceram. The seals, approximately 1″ diameter, withstood the many heating and cooling cycles demanded by the system without failure.

Tungsten leads up to .030″ diameter have been found to make satisfactory seals throughout the temperature range with No. 9606 Pyroceram. Tungsten must be properly prepared to resist oxidation at elevated temperatures. Molybdenum should also be applicable in some products but its poor resistance to oxidation must be overcome. Chromizing* may be a process which could very well overcome the oxidation difficulties of molybdenum.

For joining Pyroceram No. 9606 to itself and tungsten, Pyroceram cement No. 45 is a satisfactory medium. This provides a vacuum tight envelope which can be processed at high temperatures (750°C. bakeout) and operated for extended periods at high temperature. Work in this field especially at high temperatures, will be continued at Westinghouse with the development of a triode of suitable characteristics.

PART TWO

SELECTION & PREPARATION OF LEAD WIRES

Introduction

In vacuum tubes the d.c. and a.c. potentials and currents must be brought through the wall of the vacuum envelope to the internal electrodes. This is accomplished by conduction through suitable metal lead wires.

Part one of this paper described the positioning of two-piece lead wires within the Pyroceram envelope. A two-piece lead consists of two dissimilar metals welded together at one end. Reference hereafter will be made to inner leads and outer leads. Inner leads extend from within the envelope, through the seal area, and emerge partially exposed to the outside environment. Outer leads are joined to the inner leads at junctions external to the envelope, commonly termed "weld knots".

At 500°C. ambients, lead wires must posses certain characteristics for reliable and long lived vacuum tube operation. The coefficient of expansion of inner leads should match, as nearly as possible, the coefficients of expansion of both the solder glass and the Pyroceram No. 9606 from -65°C. to 750°C. Inner leads should maintain a low vapor pressure at high ambient temperatures to ensure absence of evaporated gases or metals poisonous to the cathode. Solder glass should easily wet and adhere to inner lead surfaces in the seal area. Inner and outer leads must withstand exposure to air at 500°C. ambients without failure caused by oxidation, brittleness, or physical weakness. The initially high electrical conductivity of both types of leads must be retained under these severe oxidation conditions. Both leads must be readily weldable to inner and outer circuits and components. Lead wires should not deteriorate in the presence of radiation.

Outer Lead Wires

The search for suitable outer leads included the investigation of the electrical conductivity, weldability, ductility, and other characteristics of over 30 metals, alloys, and cladded metals. From these, six were selected for closer examination and evaluation.

The effects of exposure to air at 550°C. of these six metals and cladded metals are shown in Table 1.

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*Chromalloy Corporation, West Nyack, New York
Alloy Surface Company, Wilmington, Delaware

EXPOSURE OF CONDUCTORS TO AIR AT 550°C.

MATERIAL SUPPLIER	DIA.	SURFACE APPEARANCE			FLEXIBILITY (1)*			CONDUCTIVITY	RESISTANCE OHMS/*Ft. at 26°C.*		
		0 Hrs.	*210 Hrs.*	*500 Hrs.*	*0 Hrs.*	*210 Hrs.*	*500 Hrs.*	*% of Copper 0 Hrs.*	*0 Hrs.*	*210 Hrs.*	*500 Hrs.*
Low Carbon Nickel (W. B. Driver)	.025″	Bright	Dull Gray-Blue	Dull Gray	7½	8½	9	20	.088	.084	.086
Low Carbon Nickel (Driver-Harris)	.028″	Bright	Smooth Blue	Dull Gray-Blue	7	7½	8½	20	.07	.07	.072
Consil-995-B Silver-Mg-Ni (Handy & Harmon)	.025″	Dull Gray	Dull Gray	Dull Gray	12	1½	1	75	.028	.032	.034
Oxalloy-28 Stainless Clad Copper Wire (Sylvania)	.020″	Smooth Blue	Smooth Blue	Smooth Blue-Gray	6½	7	6½	60	.04	.04	.04
Kulgrid-28 Niclad Copper Wire (Sylvania)	.0253″	Bright	Smooth Blue	Smooth Blue-Gray	6½	6½	5	70	.03	.028	.03
Kovar Clad Copper Wire (Carborundum Co.)	.019″	Bright	Dull Black	Dull Black	7	7	5½	12	.23	—	.23

NOTE: All samples were annealed preceding the exposure at 800°C. for 10 minutes in Ammogas.

(1)* Number of 90° bends, ¼″ span in ASTM Bending Fixture, Specification F-203-50.

From these exposure tests, Consil-995-B is seen to be unsatisfactory because it developed brittleness. Kovar-clad copper wire is undesirable because of its low conductivity. Oxalloy and Kulgrid-28 are comparative in conductivity at zero hours and do not change after exposure. Low-carbon nickel has excellent flexibility before and after exposure, but its conductivity is only one-third that of Oxalloy and Kulgrid. At 550°C. the measured conductivity of these two cladded materials is approximately 5½ times that of nickel. They are very satisfactory for conductivity, but for oxidation resistance have been found disadvantageous: (1) Complete absence of discontinuities in the surface protective layer can never be certain or guaranteed; and (2) Outer lead wires must be cut to suitable lengths, which provide possible areas of entry for oxidation at the ends between the cladded layers. Therefore, cladded lead wires were eliminated from further consideration.

Low-carbon nickel wire of 25-mil diameter was finally selected as the outer lead material. It has a fair conductivity which does not decrease during exposure, maintains its ductility, has good strength over the operating range, and is resistant to oxidation. To maintain strength and ductility it is important that low-carbon nickel should not be heated for extended periods above 800°C., since large crystal growth will result. Above 600°C. some recrystallization will occur, but not sufficiently to adversely affect strength or ductility.

Inner Lead Wires

Tungsten, molybdenum, and Kovar are well known and have been successfully used for years in the fabrication of metal to glass seals. Tungsten has a thermal expansion coefficient of about 46×10^{-7} in./in./°C. over the range of 23°C. to 700°C. The coefficient of thermal expansion for molybdenum is approximately 55×10^{-7} in./in./°C. for this temperature range. At approximately 45×10^{-7} in./in./°C., Kovar is fairly constant from 23°C. to 450°C. At 450°C. Kovar passes through a point of inflection when its coefficient increases very rapidly; it has an average thermal expansion coefficient of about 93×10^{-7} in./in./°C. over the range of 25°C. to 700°C.

From these three metals, it was decided to eliminate Kovar because of mismatch in thermal expansions. It was believed that best results could be expected with tungsten, but it was decided to explore both molybdenum and tungsten of 20-30 mil diameter.

Choice of either molybdenum or tungsten for use as an inner lead in the seal area is dependent upon adequate resistance to oxidation during sealing and tube operation. Bare leads, of course, will catastrophically disintegrate at 500°C. ambients, usually 60-86 hours in sealed envelopes. Therefore, it was necessary to apply protective barrier layers to these metals. The goal was a vacuum-tight envelope to operate at 500°C. for a minimum of 1000 hours. Inadequately protected leads will undergo either slow or rapid oxidation in the seal area so as to allow leakage of the outside atmosphere between the leads and the solder glass. The result is loss of vacuum.

Barrier layers must possess all of the characteristics for inner leads mentioned earlier in this paper. Particular care should be exercised in selecting a layer to match, as nearly as possible, the thermal expansions of the lead wire material, the solder glass, and the Pyroceram No. 9606, especially if the protective layer is of appreciable thickness. Thin protective layers do not usually present difficulties from differences in thermal expansions.

The research and development of protective layers for tungsten and molybdenum at high temperatures has accelerated, especially during the last ten years. Materials used for this purpose have been typically glass, ceramics, metal oxides, or metals. The methods of application have been electroplating, spray coating, vapor-phase coating, molten metal dipping, and cladding.

Some of the more promising electroplates are aluminum, chromium, gold, iridium, nickel-chromium, palladium, platinum, rhodium, silver, and chromium-nickel-vanadium[8].

Spray coatings can be either applied by means of cold paint-like dispersions of ceramics[9] and metals or by molten metals. Layers of powdered metal oxides of Mg, Al, Be, Th, and Zr have been used[10]. Spray coatings of aluminum-chromium-silicon, nickel-chromium-boron, and nickel-silicon-boron have been reported to be very effective[11,12,13].

Metals are frequently deposited from the vapor phase to form intermetallic alloys or diffusion coatings with the base metal[9,14,15,16]. Much work has been done with vapor depositions of Cr, Si, and Al by chromizing, siliconizing, and aluminizing.

Molten metal dips have utilized[17] aluminum and aluminum-silicon alloys [18].

Experimental

Electroplating and vapor-phase coating methods of application were chosen for consideration. The principal advantage of these methods lies in their ability to limit the barrier to a thin layer of rather high density.

Vapor-phase coatings were deposited on molybdenum and tungsten to form diffusion layers of silicides[19]. Tungsten was so severely embrittled as to render it useless; it could not be bent without breaking. Molybdenum did not appreciably embrittle. Treated tungsten was badly oxidized after exposure for 24 hours at 600°C. in air. Treated molybdenum showed only traces of oxidation after the same exposure. No seals in envelopes were made with silicided molybdenum. Limited tests with sealed chromized tungsten leads were unsuccessful because of initially leaky seals.

Electroplated gold and platinum on tungsten were selected for evaluation. Gold is unique in that it forms no oxide at any temperature. Platinum does not undergo rapid oxidation until 1620°C., but has at times been suspected to be fairly permeable to air. The rate of diffusion of oxygen through gold is believed to be very low.

Platinum plated tungsten yielded initially leaky seals, and further testing was discontinued.

A 0.1 mil electroplated layer of gold on tungsten proved to be a very effective barrier layer. Gold deposited on and diffused into a very thin nickel strike layer was less effective for oxidation prevention and gave, for the most part, initially leaky seals.

As expected, accelerated oxidation tests at 700°C. with 0.1-0.8 mils of gold revealed that oxidation resistance increases as the thickness of the electrodeposit is increased. Because the thermal expansion of gold is 142×10^{-7} in./in./°C., it was deemed necessary to minimize possible deleterious expansion effects by evaluating 0.1 mil deposits.

Further oxidation resistance was gained by application and sintering of thin layers of potassium silicate or borax to gold plated tungsten. The value of these applications was clearly demonstrated with unsealed leads by oxidation tests at 700°C.; but, no detectable evidence of increased resistance of leads sealed into vacuum envelopes was noted after environmental tests at 500°C.

Using two-piece leads of 20-mil low-carbon nickel and 20-30 mil centerless ground tungsten, the following plating procedure was developed and used through most of the project:

1. Vapor degrease in trichloroethylene.
2. Ultrasonically degrease in trichloroethylene.
3. Electropolish at six volts d.c. in 10% by weight sodium cyanide until a bright, leveled surface is obtained, usually 30-60 sec. Rinse in deionized water. Electropolishing not only provides a clean, active surface for electrodeposition, but is inherently less susceptible to initial leaks.
4. Strike 60 sec. at approximately five asf. in a bath composed of 75 g/l of potassium cyanide and 2 g/l of potassium gold cyanide. Occasionally agitate the leads and operate the bath at room temperature. Rinse in deionized water. Oven dry at 120°C.
5. Sinter for five minutes at 800°C. in ammo gas to obtain adherence of the deposited gold.
6. Electroplate for 10 minutes at 3.5 asf. in a bath composed of 20-30 dwt/gal. of potassium gold cyanide, 4 oz./gal. of potassium cyanide, 2 oz./gal. of potassium carbonate, and 4 oz./gal. of dipotassium phosphate. Operate a still bath at 55°-71°C. Rinse in deionized water. Oven dry at 120°C.
7. Sinter the electrodeposit for 10 minutes at 800°C. in ammo gas. The thickness of the electrodeposit is approximately 0.1 mil.
8. Heat the leads just below red heat and dip into a hot (40°C.) 1:1 mol ratio potassium silicate solution (26% solids) diluted with three volumes of water.
9. Oven dry at 120°C. for 16 hours.
10. Sinter at 800°C. for five minutes in ammo gas.

Conclusions

Results of life test data with 0.1 mil gold plated tungsten leads were quite conclusive. Leads intact with vacuum-tight envelopes will survive for at least 5000 hours at 400°C. Failures were observed, as evidenced by leaks, between 1400-1500 hours at 500°C. ambient temperatures.

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THE TECHNOLOGICAL TRAINING OF EUROPEAN LAMPWORKERS

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An inquiry into European methods of training Scientific Glassblowers was conducted as part of the author's 1960 Summer Vacation. The material mainly concerns training as practiced in Great Britain, Holland, and West Germany, and includes some comments on the Industry throughout Western Europe.

INTRODUCTION

In order to acquaint North American readers with details of European educational practices, it will first be necessary to give some comparisons and "translations", matching the terms and expressions which define the progress and abilities of individual students.

PRIMARY EDUCATION

As a general rule, the European scholastic system is similar to its North American counterpart for students up to the age of eleven (or a little earlier in some cases). At this crucial time, the student body is diverted into two distinct streams. Sorted by means of competitive examination, about 25% will be given a formal education directed toward entrance into a College or University. The remaining 75% will attend a so-called secondary school in which they will receive teaching and disciplines directed toward local interests and well-rounded development.

Around the ages of fourteen to sixteen, the students of the latter group are given the opportunity to attend a technical school, which corresponds roughly to the Vocational School, and has a three-year course; in England about 8% of secondary students will continue on to this school, the balance will cease full-time education entirely.

It is from this technical group that Industry elects to draw many of its potential Supervisors and Foremen. Here are also formed the craftsmen and technicians who participate in the present day Research Industry.

So much for a rough outline of early education.

FURTHER EDUCATION

As is well known, the European craftsman has always had a tradition of apprenticeship. This is generally obtained in two ways.

1. Continuation at a Technical College or Polytechnic Institute.
2. Training within a Business establishment as a full-time employee with the right to continue an education on a part-time basis.

Colleges catering to this type of student award nationally recognized diplomas at various stages of advancement, which reflect the student's competence in each subject studied.

To give an example; the "National" certificate offered at most English colleges will reflect competence in Chemistry, Physics, and Mathematics with a subdivision within stressing *one* of these subjects. Thus, it is possible to attain

Degree equivalent in Physics with only a minimum requirement in the other subjects.

As can be seen, such a scheme is designed to meet the needs of the Technician who specializes. However, it is important to note that all sorts of combinations can be taken, all leading to an external degree awarded by a reputable University. Summed up, anyone can achieve degree status, though not necessarily by full-time attendance at a University.

It is with this background in mind that it is necessary to approach the methods by which the European Glassworker is trained.

HISTORY AND GEOGRAPHY

The main centers of laboratory glassworking in Europe are to be found in Germany, England and Czechoslovakia. Smaller industries are to be found in Italy, Holland, France, and Sweden. All of these countries are noted for their much larger industrial-ware production.

The art of Lampworking would appear to have spread from Italy, where the artistic and novelty "pipe" workers made the occasional retort and reaction bottle, to Bohemia and Thuringia (in what is now Eastern Germany), and Czechoslovakia. Here, traveling craftsmen and farmworkers made small novelties and, upon special request, scientific apparatus.

As the progress of experimental research increased, an industry was created, which in turn dominated world supplies until 1914. At that time, England and the United States were called upon to create new programs from scratch. Of the countries mentioned, Sweden appears to be the isolated case of Europe. Although of long standing, its lampworking industry appears to be of minor importance.

The primacy of Germany, England and Czechoslovakia is related to the size and productive capacity of the Schott-Jena, Pilkington, and Cavalier Industrial complexes, respectively, which approach the Corning and Kimble works of the United States in diversity. Many skilled craftsmen, trained in these works, have launched out as specialty manufacturers and created a network of subsidiary enterprises, all of which compete for skilled labor.

In order to ease this situation, it has been the policy to create Technical Schools in which basic training is provided and coupled with technical knowledge. In Germany, the school system originally centered in Thuringia, has, since partition in 1945, been re-established in the Western Zone.

DISCUSSION

Since any discussion concerning lampwork will inevitably involve the debt owed to those unknown German craftsmen whose ingenuity and skill started the craft as we know it today, it is fitting that this discussion commences with an appraisal of the German school.

For many years, the official diploma-awarding body has been at Heidelberg. Any individual wishing to upgrade his skill to that of Master Glassblower in the laboratory (or Laborglas) field, would apply to the Technical Institute for permission to sit their examination. In this respect is seen the part-time character of the training. However, on the lower level, if one attended the "Schule Laborglas" situated at Ilmenau in Thuringia, it was recognized that the trainee was of medium-grade caliber, measured on a scale consisting of Improver, Intermediate, and Master Glassworker. All others trained at other establishments were only recognized by their possession of the Heidelberg diploma for each of the above-mentioned grades.

Since 1945, when a large number of executives and craftsmen fled to the Western Zone of Germany, the laboratory glass industry has been located at Wertheim am Maintz in Bavaria. With perhaps the exception of Schott of Jena glass fame, now relocated in the town of Maintz to the north of Wertheim, more glassware of all descriptions is manufactured in this small country town than anywhere else in Western Europe outside of England. It would not be an exaggeration to say that anything which commences with tubing as its raw material is or can be made in one or other of the sixty or more firms located here. In addition to the laboratory glass firms, two large Glassworks (Glasshutte) serve as the basic source of raw material and individually produce significant amounts of finished products. As a result, it was natural for the authorities to also locate the new training school in this area.

Established in 1950, the Bundesfachschule fur die Glasinstrumententechnik of Wertheim is the direct inheritor of the Ilmenau school, now in the Eastern Zone of Germany. The established object is to train promising young glassworkers in the art of lampworking and the associated technology. Supported entirely by Provincial (local Government) funds, no help other than the supply of raw materials (free) is accepted from Industry in order to preserve autonomy.

To enter the school, the potential trainee is required to show evidence of about three years experience within a recognized business or service under a master glassworker. There is an entrance examination to prove a certain degree of aptitude and, if satisfactory, the student will then be enrolled with the prospect of attending four semesters of six months' duration.

The translation to English of the published curricula provides the following information.

CURRICULA:

		Semester		
1. *General Courses*	I	II	III	IV
German Language	2	2	2	2
Law and Sociology	1	1	1	—
Mathematics	2	2	2	2
Technical Arithmetic	1	1	1	2
2. *Technical Courses*				
Instrument Knowledge	3	3	3	3
Physics	4	4	4	4
Chemistry	2	2	3	3
Technical Drawing	3	3	3	3
3. *Commercial Courses*				
Grammar and Composition	1	1	1	1
Elementary Economics	1	1	1	1
Price Calculation	—	1	1	1
Bookkeeping	—	—	2	2
Geography	—	—	1	1
Personnel Relations	1	1	1	1
4. *Practical Courses*				
Laboratory Instruction	20	19	16	16
Total hours per week	41	41	41	41

Summer Semester—1 March to 31 July.

Winter Semester—20 September to 20 February.

Included in the Laboratory Instruction period are allowances for visits to the Glass Industry, both in Germany and abroad in England, Holland, and other neighboring countries.

According to a discussion the author had with a school representative, the courses are not pure subjects, but in all cases are slanted with emphasis on practical requirements. For example,

a) Physics as listed emphasizes radio tube construction, etc.
b) Chemistry as listed emphasizes laboratory experimental equipment.
c) Mathematics and Technical Arithmetic reflect ability in Trigonometry, Geometry, Algebra and Arithmetic as applied to jig construction, machine shop practice and so on.

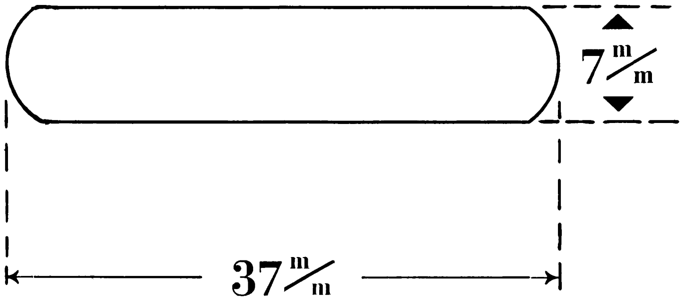
As further evidence, an examination paper from another, similar establishment at Leiden, Holland, is reproduced below. It contains both theory and practice and can fairly be said to represent the approximate overall standard expected of trained glassworkers.

Of the three stages of aptitude recognized, *i.e.*, Improver, Intermediate, and Master, these papers are set for the latter two groups by a competent examining body, and marked independently. The practical examples are compared against a master specimen and deductions made for faults.

INTERMEDIATE AND MASTER EXAMINATION 1959.

General (1¼ hr.)

1a. What is the volume of the cylinder as sketched? The ends are purely spherical, and internal measurements are given. The overall length is 37 mm. (For π, use 22/7 and no slide rules, tables, etc., are allowed.)



1b. What is the weight of a glass tube diameter 140 mm., length 600 mm., wall thickness 3 mm.? The specific gravity of the glass is 2.6.

2. To determine the specific heat of brass metal, 27 grams of this metal at 100° Celsius is placed in a calorimeter containing water at a temperature of 18° Celsius. The water value of the calorimeter is 100. The temperature of the calorimeter rises 2° Celsius after the brass is placed in it. What is the specific heat of the brass?

3. What is the numerical value of:

a) Cos 45°, b) sin 30°, c) tan 60°,

d) Simplify

$$\frac{1}{1 + \tan^2 a} + \frac{1}{1 + \cot^2 a} - (\sin^2 a - \sin^2 a \cos^2 a)\ (\tan a + \cot a)^4 \cdot \cos^4 a.$$

No tables to be used.

4a. Name three methods of heat transfer phenomena.

b. What determines the pitch of a tone?
(Author's Note—*i.e.,* What is the relationship between frequency produced and length of vibrating string?)

c. What is the principle of operation of an amp meter? Give a sketch and show how it is incorporated in a circuit.

d. Calculate the current through a lamp of 200 watts rating fed from a 220 volt power line.

5a. Give the chemical equation expressing the reaction of sulphur and iron when heated together. Name the end product.

b. With how many grams of iron will 16 grams of sulphur react when the atomic weight of iron is 55.8 and that of sulphur is 32?

c. Give the chemical equation for the reaction of oxygen and hydrogen.
How many grams of oxygen will combine with 5 grams of hydrogen given their respective atomic weights as 16 and 1, respectively.

d. Express in chemical symbols the formula for
1) Sulphuric acid; 2) Calcium Carbonate; 3) Copper Sulphate (hydrated); 4) Methane; 5) Ethyl Alcohol.
Derive the full names of the following compounds:
1) $Pb(NO_3)_2$; 2) H_2S; 3) $NaOH$; 4) C_6H_6; 5) C_2H_6?

INTERMEDIATE AND MASTER EXAMINATION 1959

Practical (2 hrs.)

1. Sketch an apparatus for the vacuum distillation of contaminated mercury metal. It should possess the following features:
   a) Water cooled.
   b) Metal can be continuously removed or replenished without halting the distillation.
   c) The distilled metal must be free of water contamination.
   The drawing must be so set up that it can be used in shop production.

Theory (2½hrs.)

1. A burette of 50 ml. capacity has to be calibrated and etched to 0.1 ml. precision. How would you divide and etch these markings? What materials would you use and what precautions would you adopt to avoid "rejects" and operator injury?

2a. Give one method of sealing tungsten to glass.

b. Give the code name of a glass of matching characteristics.

3. What is tempered glass and how can it be produced?

4a. Which glass has the highest specific gravity value—
Pyrex (Corning) or Lead glass (Jena)?

b. Give an approximate value for Lead glass.

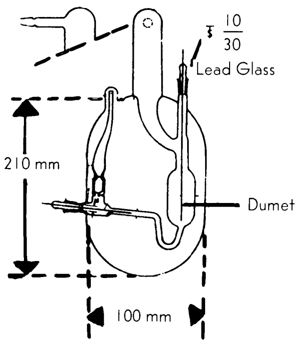
5. What is an "Aerometer" and how does it operate?

6. Name one glass that will transmit "u.v." light as one of its major characteristics.

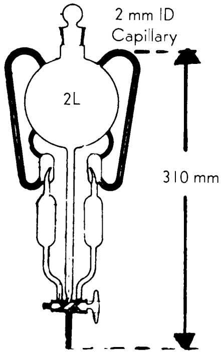
7. What are the effects of the electrical resistance and water absorption on glasses used in vacuum tubes?
8. Give a brief description of the operation of a "Contra-barometer".

Practical Laboratory (Master)

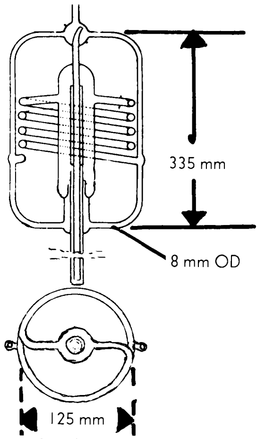
The following are to be made within the time listed and are judged on finish, accuracy of dimensions and knowledge of operation. All measurements are in metric units.



Pyrex Manostat
Time 10 hrs.



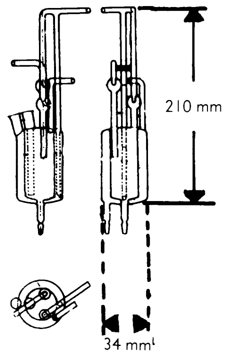
Pyrex Double Pipette
Time 16 hrs.



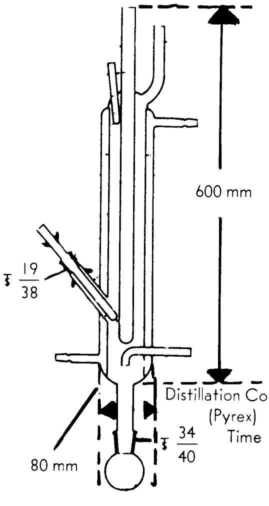
Pyrex Circulation Pump
Time 8 hrs.

Practical Laboratory (Intermediate)

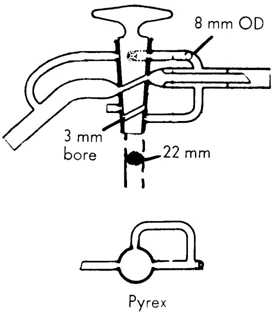
The following are to be made within the time listed and are judged on finish, accuracy of dimensions and knowledge of operation. All measurements are in metric units.



Soda Lime Manometer
Time 8 hrs.



Distillation Column
(Pyrex)
Time 15 Hours



Pyrex
Multi-bore
Stopcock
Time 9 hrs.

The writer was not able to obtain copies of the examination in metal work, bookkeeping, etc., but it is safe to assume that the standard is approximately comparable to that taught in the higher grades of the North American vocational school.

As can be appreciated, the curricula is wide and constitutes a strong base from which the potential supervisor can work. At this point, it is of interest to take note that the theoretical quesions asked of he Wertheim-diploma aspirant are possibly a little more complex than the Leiden examination, since the latter institute aims primarily to train first-grade craftsmen, not supervisors. Consequently, due to this policy, the standard of workmanship demanded at Leiden appeared to be a little more stringent.

Germany, as in the past, has a large industry based on Laboratory glass, and since the economy thrives by exports, it has been necessary to invest heavily in human resources of high caliber. All lampworkers in Germany have the opportunity for equal technical education and are well-equipped to withstand the effects of automation and mass-production changes.

SOME OTHER PROGRAMS

Comparable with the German scheme, similar schools exist in many of the other prominent glass-producing countries, notably the above mentioned Leiden in Holland.

Additionally, in all the countries mentioned, classes are organized for *anyone* interested in glassworking and are generally run in conjunction with a recognized technical course for which it supplies an optional credit. For example,

a) The English medical-laboratory technician is required to reach improver standard in glassblowing.

b) Science-school teachers find it convenient to be taught the basic methods of glasswork.

As in the United States, some Universities in Europe have developed programs on a selective basis for training full-time apprentices, holding select courses in higher techniques and also demonstrating basic techniques to Post-Graduate Researchers and Laboratory Technicians. The larger Chemical and Electronic ware manufacturers also train their own craftsmen and demand a knowledge of theory as the passport to advancement.

CONCLUSION

In our present society, where rapid technical change overtakes techniques, men and jobs in a few years, even months, as compared to the decades of only a generation ago, individual groups cannot afford to stand still. Since the Second World War, many operations formerly done by hand have been mechanized. Perhaps as in other industries that have expanded, the common laboratory article will eventually be completely produced by mass-production methods. This naturally creates a demand for designers or technologists who know what can be achieved with the basic material in terms of functional use and potential.

Already individual Research establishments require technical personnel who can plan, erect and initially operate various complex systems. To the author, it seems highly desirable that there should exist in the United States an institution where all phases of glasswork could be taught. There exist many schools for the practice of ceramics and pottery, but apparently none for glassware. Perhaps the members of this Society will discuss this apparent omission and find some merit in the idea.

ACKNOWLEDGMENTS

The author places on record his appreciation of the cooperation and advice, often at short notice, from the following.

1. Dr. A. Klein, Area Director, Glass Council, Wertheim.
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5. J. Burrow and R. Garrard, Bristol University, England.
6. S. G. Yorke of "Quickfit and Quartz", England.

ANNEALING OF GLASS—THE PRACTICAL APPROACH

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ABSTRACT

Much has been written about the temperature cycles required to anneal glass. However, most of the specific information in the literature is about the annealing of optical glass where extremely low stresses are necessary. These cycles are long and are not usually required for either glass products. Typical annealing cycles were given for various glass products. Some of the problems of glass annealing were discussed including the use of stress in the glass to strengthen the article.

LOW TEMPERATURE SOLDER GLASSES IN THE ELECTRON TUBE INDUSTRY

J. L. GALLUP
R.C.A., Harrison, N. J.

This is a discussion of some of the uses of low melting solder glasses in the electron tube industry. Properties of certain glasses in the lead-boro-silicate system are described. Photographs depicting some actual commercial products sealed with these glasses are reproduced.

INTRODUCTION

Definition

For a number of years, glasses with low-temperature softening ranges, 600°C. and below, have been used in the electronics industry to join glass parts to each other, to metal and to ceramic parts at temperatures previously used only for metal solder seals. Hence, these glass sealing materials have come to be called "solder glasses."

Literature

The lead-boro-silicate system which will be considered here has received extensive investigation at the National Bureau of Standards and elsewhere. References to this literature are included in the bibliography at the end of the present paper.

LEAD-BORO-SILICATE GLASSES

Preparation

The glasses are prepared from chemically pure boric acid, red lead and silicic acid. The glasses used for analyses, viscosity measurements and thermal expansion measurements were melted in a platinum crucible in 200 gram melts. The crucible was heated by placing it in an air furnace at appropriate temperatures between 700° and 1100°C., depending upon the composition. During the three hour melting period, the melts were repeatedly stirred with a platinum rod to obtain uniformity.

In the case of the glasses used in the commercial products shown in the slides, the glasses were melted in batches of several pounds in large fused quartz crucibles. The glass was quenched by pouring on large steel slabs. It was then reduced to a fine powder by first crushing the pieces in a jaw crusher, followed by milling the eight mesh fragments in a porcelain ball mill to pass a 150 mesh screen.

Compositions

The low melting glass compositions considered are shown in Table I.
The weighed batch compositions check well with the results of the chemical analyses. This indicates that the loss of ingredients through volatilization during melting is small.

Viscosity

Viscosity measurements were made at several temperatures corresponding to viscosities in the range from $10^{9.5}$ to $10^{13.5}$ poises. Data for the softening point at $10^{7.6}$ poises and the strain point at $10^{14.6}$ poises were obtained by extrapolation.

TABLE I

Compositions
(Per Cent by Weight)

No.	PbO Chem.	PbO Batch	B_2O_3 Chem.	B_2O_3 Batch	SiO_2 Chem.	SiO_2 Batch
1	71.4	71.3			28.6*	28.7
2	84.8	84.7			15.2*	15.3
3	76.3	76.2	23.7*	23.8		
4	82.8	82.7	17.2*	17.3		
5	88.3	88.0	11.7*	12.0		
6	71.9	72.0	14.2*	14.0	13.9	14.0
7	85.1	85.0		7.5		7.5

*By difference

Measurements of viscosity were made by the fiber-elongation method in which the rate of elongation of a fiber held at various temperatures under known loads is determined. The apparatus used was similar to that of Boow and Turner.[8] Theory and technique of measurement have been described by Lillie.[9]

The results are shown in Table II.

TABLE II

Viscosity Data
(Poises)

Composition Mole %	$10^{7.6}$* Softening Pt. (°C.)	$10^{13.4}$ Annealing Pt. (°C.)	$10^{14.6}$* Strain Point (°C.)	10^{9} (°C.)	10^{10} (°C.)	10^{11} (°C.)	10^{12} (°C.)
40 PbO, 60 SiO_2	568	444.0	421.5	535.5	512.0	490.5	471.0
60 PbO, 40 SiO_2	429	375.5	344.5	410.0	397.0	384.5	373.0
50 PbO, 50 B_2O_3	435	376.5	365.5	419.0	408.5	398.0	389.0
60 PbO, 40 B_2O_3	383	327.0	317.0	368.0	357.5	348.0	339.5
69.5 PbO, 30.5 B_2O_3 .	330	281.5	272.5	317.0	308.0	300.0	292.0
42.7 PbO, 26.5 B_2O_3, 30.8 SiO_2	477	406.5	393.5	458.5	445.0	433.0	421.5
62 PbO, 17.6 B_2O_3, 20.4 SiO_2	371	311.0	300.0	355.0	344.5	333.5	324.0

*Extrapolated from measured values.

Table III compares solder glass and two standard soft glasses at three standard viscosity levels.

TABLE III

Comparison of Solder Glass and Standard Glasses for Viscosity

Glass	Softening Point	Annealing Point	Strain Point
#6 Solder Glass	477	406.5	393.5
0080 Lime	696	510	478
0120 Lead	630	433	400

Although the #6 solder glass is only 6.5°C. below the standard lead stem glass in strain point temperature, so rapid is its change in viscosity that the difference at the softening point is 153°C. This rapid change in viscosity gives the solder glasses a relatively short working range and explains their high fluidity at low temperatures. It is this high fluidity at low temperatures which allows the solder glasses to fuse to the standard glasses before the latter become soft enough to deform.

Thermal Expansion

Thermal expansion measurements were made in an automatic dilatometer* of the quartz-expansion-furnace type. A four-inch long sample was used. It was prepared by casting from molten glass into a metal mold heated on a hot plate. Samples were heated at a rate of 4°C. per minute until the four-ounce pressure of the dial gauge spring caused the sample to stop expanding vertically. The sample was then cooled at a rate of 2°C. The coefficient of thermal expansion was calculated from the cooling curve for the range from room temperature to 300°C. Table IV gives the values calculated for the compositions considered.

TABLE IV

Coefficient of Thermal Expansion of High Lead Solder Glasses

	Composition		Coefficient of Thermal Expansion 30° to 300°C.
	Mole (%)	Weight (%)	
(1)	40 $PbO \cdot 60\ SiO_2$	71.3 PbO, 28.7 SiO_2	74 x 10^{-7} in./in./°C.
(2)	60 $PbO \cdot 40\ SiO_2$	84.7 PbO, 15.3 SiO_2	108 x 10^{-7}
(3)	50 $PbO \cdot 50\ B_2O_3$	76.2 PbO, 23.8 B_2O_3	93 x 10^{-7}
(4)	60 $PbO \cdot 40\ B_2O_3$	82.7 PbO, 17.3 B_2O_3	108 x 10^{-7}
(5)	69.5 $PbO \cdot 30.5\ B_2O_3$	88 PbO, 12 B_2O_3	124 x 10^{-7} (only to 280°C.)
(6)	42.7 $PbO \cdot 26.5\ B_2O_3$ 30.8 SiO_2	72 PbO, 14 B_2O_3, 14 SiO_2	85 x 10^{-7}
(7)	62 $PbO \cdot 17.6\ B_2O_3 \cdot 20.4\ SiO_2$	85 PbO, 7.5 B_2O_3, 7.5 SiO_2	117 x 10^{-7}

Glasses 2, 3 and 5 have been used as the cementing agent in permanent marking inks stamped on the bulb walls of soft glass electron tubes having thermal expansion coefficients of about 90 x 10^{-7} in./in./°C. The lack of difficulty in using these three inks makes it appear that coefficient of thermal expansion is not critical for solder glasses applied in thin layers over limited areas.

Glasses 6 and 7 have been used to seal 0120 glass stems to cold rolled steel shells. Glass 7 provided a better match and gave better results.

Glass 6 has been used in sealing mica to 0080 or 0120 glass bulbs and to steel shells. Glasses similar to 6 have proven valuable in sealing lime glass diaphragms to chrome iron rings where close expansion matches were necessary.

Uses of Solder Glass Seals

Solder glasses such as these which have been described have been and can be applied to many sealing situations in the electron tube industry. However, their primary advantage is their low softening temperature and hence, the relatively low temperature at which vacuum-tight seals can be made. Such low sealing temperatures are primarily valuable in situations where metal parts are close to the seal area and likely to be deformed or oxidized by the heat required to seal the normal standard glasses.

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*Automatic Recording Dilatometer, Type 135. Made by Sylvania Electric Products, Inc., Electronics Division.

Solder glasses are usually applied in powder form either as a dry powder sifted on a hot metal part or as a liquid suspension painted on the parts to be joined and subsequently heated to fuse the powder. If the dry powder technique is used, the powder is used in a carefully sized range, usually 40 to 100 mesh material, in order to avoid producing a toxic air-floated dust.

When a liquid suspension is used, the powder is ground finely in a ball mill (200 mesh or finer) in a liquid such as methanol or water. The resulting suspension can be applied by brushing or spraying. If the particles have been ground down to contain many particles in the ½ micron range, the suspension will settle very slowly. Otherwise, it will have to be stirred repeatedly, since the high density (five to seven times that of water) causes large particles to settle rapidly. The small particles in the ½ micron range are kept in suspension by Brownian movement.

Photographs Showing Solder Glass Uses

Figure 1 shows a miniature tube with the type number composed of solder glass bonded marking ink. It has been applied by rubber stamping from a finely ground suspension of solder glass in glycerine. It is fused in place when the bulb passes through gas flames on a rotating tubulating machine.

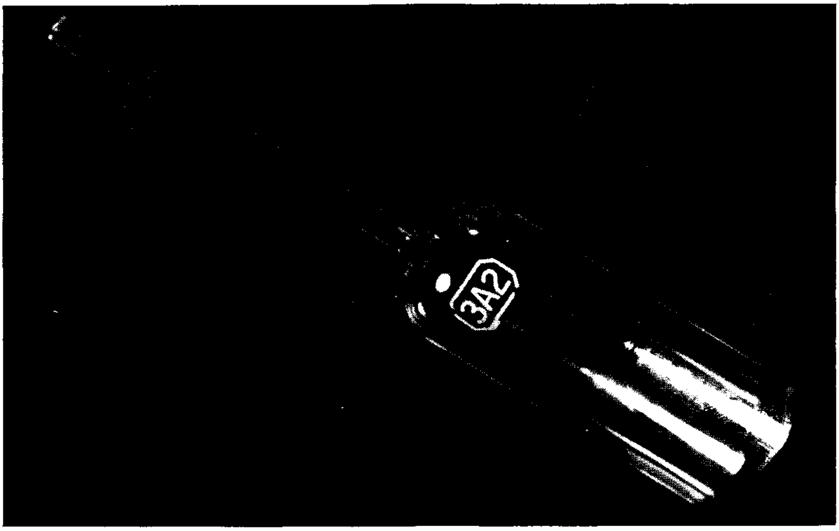

Figure I
Glass Marking Ink

Figure 2 shows two views of a record playing stylus tube. The solder glass which seals the tube is applied as a dry powder sifting against the hot inside lip of the rotating metal shell. The glassed shell is then sealed to the stem containing the mount by a small flame directed against the outside of the metal shell lip.

Figure 3 depicts a mica-to-metal seal in a magnetron window cup. The mica must be kept below 600°C. during sealing in order to minimize decomposition of the mica. The use of a solder glass allows this to be done.

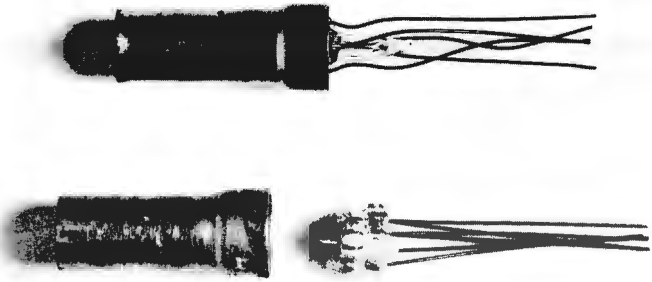

Figure 2
Transducer Tube

Figure 3
Mica to solder glass to metal seal

In Figure 4, there appear two views of a metal ring used to support the thin glass target diaphragm of an image orthicon television pickup tube. The solder glass which cements the higher melting glass of the target diaphragm to the ring is applied by spraying. The fragile diaphragm is then laid over the ring and fused in place at a temperature which does not soften the diaphragm glass.

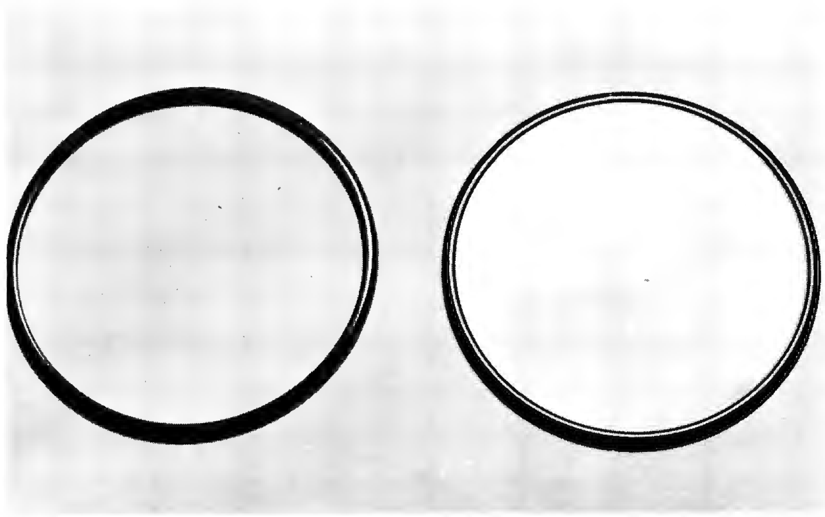

Figure 4
Glassed target ring seal

SUMMARY

Solder glasses with working or sealing ranges from 400° to 600°C. have proven valuable in electron tube construction where the higher working temperatures of the standard sealing glasses would deform, oxidize or decompose parts of the mount or envelope.

The composition and properties of seven such low melting solder glasses have been described and discussed together with comments on their use.

Four commercial examples of uses of these glasses have been described and illustrated by photographs.

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RADIATION DAMAGE IN GLASS

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USASRDL
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This paper is the result of a recently completed study which Chatham Electronics was contracted to make under the direction of the U. S. Signal Corps at Fort Monmouth, New Jersey. The purpose of this contract was to investigate the causes of radiation damage occurring in most hard glasses, and to evaluate possible replacement glasses for the hard glass electron tubes used in military applications.

There is a logistic need in military operation for electronic equipment to remain operative in the immediate vicinity of an atomic explosion or high nuclear radiation source.

The three effects of radiation on borosilicate glass are: actual glass fracture, gas evolution, and discoloration. Although the degree of discoloration does seem to be related to the likelihood of glass fracture, discoloration itself does not impair the usefulness of electron tubes with the possible exception of photo sensitive tubes. For this reason the study was directed toward the problems of glass fracture and gas evolution.

When dealing with radiation damage in glass we need only concern ourselves with two forms of radiation: namely, gamma rays and neutrons. Other forms of radiation such as alpha particles, beta particles, positrons, protons and so forth are so easily shielded that: first, they are not likely to be present, and second the outermost layer of a glass envelope itself would be sufficient to virtually stop all of these particles. On the other hand, both neutrons and gamma rays are highly penetrating and are not easily screened out. Neutrons may be subdivided into two categories: fast neutrons with energies as high as several MEV and slow neutrons possessing on the average only 1/40(1) of one ev. These low energy neutrons are referred to as thermal neutrons because their energy is primarily thermal energy. That is, their energy is determined by the temperature of the surrounding medium and is roughly the same as the average energy possessed by other atoms or molecules in the medium.

Probably the greatest cause of radiation damage in glass is the reaction of these thermal neutrons with the B^{10} isotope found in all borosilicate glasses.

It is not likely that gamma rays and fast neutrons contribute in the same degree to glass damage for the following reasons: The gamma rays, which are electromagnetic radiations similar to X-rays but generally of shorter wave length,(2) interact only with the electronic structure of the atoms. Some chemical and structural changes may result from the ejection of electrons due to the absorption of gamma rays, but the resulting damage is slight because the nuclear structure is not altered.

Neutrons, because of their lack of electronic charge, are easily able to pass through the intense electrostatic nuclear fields and interact with nuclei of virtually all elements. In the case of fast neutrons these interactions normally involve elastic collisions with the target nuclei in much the same way as two billiard balls colliding.(3) Some energy is transferred to the nuclei involved, but in these elastic collisions actual changes in the nuclear structure rarely occur. However, very low energy or thermal neutrons are highly susceptible to radiative capture. When these thermal neutrons pass through a substance containing an isotope with a large capture cross section for thermal neutrons, numerous nuclear reactions take place. In the case of thermal neutron bombardment of a typical borosilicate glass the boron nuclei react with the neutrons in such a manner as to completely disrupt the normal nuclear structure. In particular the B^{10} isotope, which constitutes about 1/5 of the naturally occurring element boron(4) used in most hard glasses, reacts with the incident neutrons in the following manner:

$$\underset{(.025\text{ev})}{{}_0n^1} + {}_5B^{10} \rightarrow {}_3Li^7 + {}_2He^4 + 2.8\text{ Mev}$$

The 2.8 Mev reaction energy is carried off by the lithium nucleus and α-particle. It is interesting to note that this neutron with 1/40th of one electron volt of energy is able to produce a reaction liberating energy in excess of 2 Mev. This reaction energy can be found by use of the Einstein equation with which you are all familiar, $E = mc^2$. The sum of the masses on the right side of this equation is less than the sum of the masses on the left by 5×10^{-27} gm. Multiplying this difference in mass by the speed of light squared gives us 4.48×10^{-6} ergs or 2.8 Mev. As already mentioned, neutrons react with virtually all nuclei but the boron reaction is of particular importance because of the large capture cross section of the B^{10} isotope for thermal neutrons. The capture cross section of a nucleus is really a measure of the probability of a given reaction. If one neutron per unit area were to strike a substance containing one B^{10} atom per unit area projected at the surface the probability of any one of these neutrons reacting with a B^{10} nucleus would be 3990×10^{-24}.(5) While this reaction may appear to be a highly improbable occurrence, it is actually an extremely frequent occurrence when we consider a dense neutron beam incident on borosilicate glass containing large numbers of B^{10} atoms.

A comparison of the capture cross section of the B^{10} isotope with some of the other elements found in glass might better illustrate this point: a neutron reaction is approximately 8,000 times less likely in sodium, 12,000 times less likely in aluminum, 30,000 times less likely in silicon and 19,000,000 times less likely in oxygen than in boron^{10}.(6)

The significance of the neutron reaction with boron^{10} lies in the fact that: first; there is a depletion of boron which might cause lattice defects; and second, there is the production of two highly ionizing particles the lithium nucleus and a helium nucleus or α-particle.(7) Because these particles appear as stripped atoms or atoms having no electrons they produce intense ionization in their tracks as they carry off the 2.8 Mev reaction energy. This ionization tends further to induce structural changes in the glass. Also, because the range of these particles is very short (only a few microns in glass) the 2.8 Mev reaction energy is dissipated within a very small volume, resulting in "thermal spikes" or intense local heating.(8) If there is a sufficient number of these reactions occurring in a glass vessel which is under strain, fracture will result.

Before looking at the experimental data I would like to go over the terminology used for exposure to neutron bombardment.

N = number of neutrons/cm^3
V = velocity (cm/sec.)
T = time (sec.)
NV = number of neutrons/cm^2 sec.
NVT = number of neutrons/cm^2

When we speak of neutron intensity or flux we express it as NV which is merely the number of neutrons striking each square centimeter of the target per second. Normally neutron dosage is expressed as NVT and is called the integrated neutron flux. NVT is the total number of neutrons incident on the target per cm^2. The normal exposure period in the Brookhaven reactor is twelve days, which is just a little more than 10^6 seconds. Thus, if a total exposure of 10^{16}NVT were requested we would expect the Brookhaven staff to position the samples in the pile so as to expose them to 10^{10}NV or ten billion neutrons striking each square centimeter of the sample per second.

Let us now turn to the experimental findings. Several glass enclosures each of Corning types 0080, 0120, 7720, and 7052 were exposed to an integrated thermal neutron flux of 10^{16}NVT. None of the enclosures showed any cracks but we see considerable differences in discoloration. (Figure 1) These enclosures were sparked with a Tesla coil and no ionized gas was visible, although the degree of discoloration in the nonex and 7052 made this method of detection extremely unreliable. Dummy bulbs of these same glass types with leads were also exposed to 10^{16}NVT. Cracking was evident only in the 7052 enclosures with molybdenum leads.

To determine the neutron flux level at which cracking starts in a typical borosilicate glass, nonex enclosures were subjected to various integrated fluxes. Cracking was observed at or above 10^{17}NVT.

Work then proceeded to an evaluation of possible replacements for the borosilicate glasses. Low boron content glasses such as Corning's 1723 aluminosilicate glass and Owens-Illinois boron-free 51-26 glass were evaluated for damage caused by neutron bombardment. Enclosures of these glasses showed no other effects than a slight brown discoloration after exposure to 10^{16}NVT. Owens-Illinois' experimental glasses containing 3% and 6% B_2O_3 showed similar results. Earlier measurements made by Owens-Illinois on irradiated enclosures of 51-26 (now called EE-2) boron-free glass showed sizeable increases in gas pressure, but we were unable to observe gas in subsequent enclosures after exposure to as much as 5.77×10^{18}NVT. Samples of these various enclosures after exposure to 9.2×10^{16}NVT are shown in Figure 2.

In an attempt to determine the relative amount of gas evolved by various glass enclosures, ionization gauges were enclosed in envelopes of Corning 0080, 7720 and 1723 glasses. The gas pressure in lime glass enclosures showed no increase after exposure to an integrated flux of 4.0×10^{16}NVT. However, the ionization gauges in 7720 and 1723 glass showed an increase in pressure from 1×10^{-6} mm before irradiation to 5×10^{-3}mm and 3.7×10^{-3}mm respectively after exposure to less than 4×10^{15}NVT.

Tests were conducted on vacuum rectifier tubes of type 5R4WGA. The tubes used were regular Chatham production 5R4's in 7720 envelopes and experimental

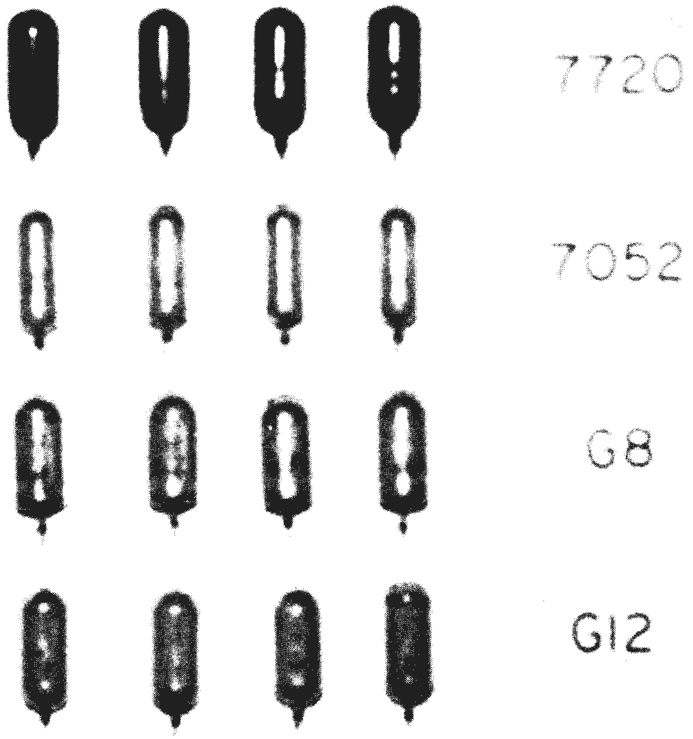

Figure I

tubes in 1723 glass. One test involved the use of nonex tubes enclosed in .007″ cadmium foil as a shield, because cadmium, like boron, has a large capture cross section for thermal neutrons. All the 5R4WGA tubes were exposed to 4 x 10^{16}NVT. The production tubes (nonex enclosures) showed large increases in plate current, but the cadmium shielded tubes had lower plate current than the unshielded tubes by approximately 25%. The 5R4's enclosed in 1723 glass showed considerably less changes than any of the nonex tubes. It is assumed that out-gasing of the glass caused the changes in characteristics. This is born out by the fact that nonex enclosures showed greater changes than 1723 enclosures much in the same way that gas evolution was more evident in nonex enclosed ionization gauges than in 1723 envelopes.

To examine the effect of strains on the fracture of glass envelopes subjected to radiation, photographs were taken on nonex enclosures through a polariscope before and after irradiation. In Figure 3 we see an enclosure with regions of extreme tension and compression. Tension appears as blue, compression as yel-

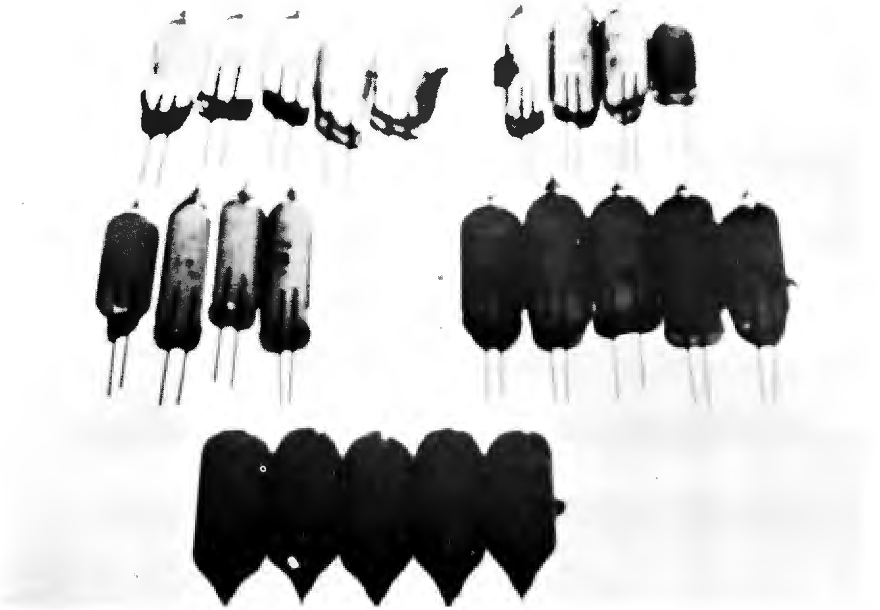

Figure 2

low. After exposure to 7.5 x 10^{17}NVT this bulb shows a ring crack at the region of greatest tension (Figure 4). A nonex enclosed 5R4 shows only slight tension near the top of the bulb (Figure 5), but after exposure to 7.8 x 10^{16}NVT we see a ring crack at that point (Figure 6).

Quantitative measurements of gas evolution were not made on Corning's 1715 boron-free glass because of the difficulty encountered in making usable stems. Dummy enclosures of this glass were exposed to 3.6 x 10^{16}NVT. Some enclosures were shielded by .005″ cadmium foil. In all cases these enclosures did show evidence of gasing up after irradiation when sparked with a Tesla coil. Only very slight discolorations were noticed and qualitative stress and strain measurements before and after irradiation indicated no changes. The only difference noted between enclosures shielded with cadmium foil and the unshielded enclosures was that the activity level after exposure was considerably lower for the shielded enclosures. Several nonex enclosures were irradiated with the 1715 enclosures as a comparison. All samples, including those shielded with cadmium, were so badly discolored that gas detection and strain measurements were not possible.

Twin triodes of type 6080WA with lime glass envelopes and 6080WB with nonex envelopes were exposed to 1.78 x 10^{16}NVT. One of the nonex enclosures was fractured during exposure. The lime glass tubes showed considerably less changes in electrical characteristics than did the remaining nonex tubes.

In summary, it appears evident that all glasses will discolor in varying degrees when subjected to integrated thermal neutron fluxes in the order of 10^{16}NVT. We have found that Kimble's EE-2 boron-free hard glass and such soft glasses as G-8 and G-12 show less evidence of gasing up when exposed to

Figure 3

Figure 4

such fluxes than other glasses tested. Ionization gauges in nonex, alumino-silicate, and lime glasses have shown that at 0.4 x 10^{16}NVT the increase in gas pressure is not more than 5 microns.

The experimental evidence appears to bear out the premise that the B^{10} isotope is instrumental in causing radiation damage to the hard glasses. Boron-free glasses exposed to integrated fluxes of up to 10^{18}NVT show no indication of fracture, while some borosilicate glasses shatter at exposures as low as 10^{16}NVT. Calculations show that only about 4/10 of one percent of the total boron content of nonex is depleted at 10^{17}NVT. It is therefore likely that fracture is *not* due solely to the depletion of boron, but may also be due to structural changes caused by the intense ionization produced along the paths of the $_3Li^7$ nucleus and the α-particle.

The increase in gas pressure in irradiated enclosures is probably due to out-gasing of the glass bulb caused by thermal spikes when the α-particle and $_3Li^7$ nucleus dissipate the 2.8 Mev reaction energy. Unfortunately, the exact temperature that the various bulbs saw in the reactor was not determined. Some samples were painted with special temperature indicating paints, but the paints themselves remained so radioactive after exposure that the samples could not be examined. Earlier measurements by the Brookhaven staff show that the temperature would be in the neighborhood of 150°C.

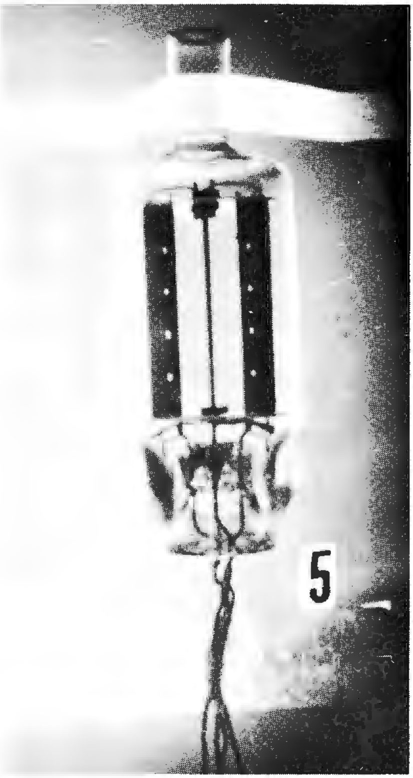

Figure 5

Figure 6

It is unlikely that α-particles themselves escape in sufficient number into the vessel to form enough helium atoms to account entirely for the increase in gas pressure. Calculations show that in nonex after an exposure of 4 x 10^{15}NVT at most only 2.0% of the increase in gas pressure could be accounted for by the formation of helium atoms from α-particles.

Although special boron-free hard glasses such as Kimble EE-2 and Corning 1715 are able to withstand extremely high neutron fluxes, we have found them very difficult to work. It would be desirable to have borosilicate glasses without the inclusion of the B^{10} isotope, but present methods of separating the B^{10} isotope from the B^{11} are so expensive as to make this impractical. Perhaps further development by glass manufacturers might result in a boron-free hard glass with working properties similar to the present borosilicate glasses.

Various shielding materials such as boron-steel alloys or cadmium foil may be used to protect present hard glass electron tubes from thermal neutron bombardment.

Wherever environmental, mechanical, and electrical conditions permit, it would be desirable to use any of the various soft glasses which are easily worked and able to withstand high thermal neutron fluxes.

NOTES

1. Harwood, Hausner, Morse & Rauch: *The Effects of Radiation on Materials,* p. 54.
2. Glasstone, S.: *Sourcebook on Atomic Energy,* p. 168.
3. *Ibid,* p. 293.
4. *Ibid.,* p. 291.
5. Hodgman, Weast, & Selby: *Handbook on Chemistry and Physics, 37th Edition,* p. 448.
6. *Ibid.,* p. 448-449.
7. Glasstone, S.: *Sourcebook on Atomic Energy,* p. 291.
8. Sietz & Wigner: The Effects of Radiation on Solids," p. 2 (Reprinted from the *Scientific American,* August 1956).

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GLASS AND METAL ULTRA HIGH VACUUM SYSTEMS

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RCA Laboratories

I. INTRODUCTION

While various systems for producing partial vacua have been known for several hundred years, high vacuum systems that yield pressures near 10^{-6} torr (mm Hg) were only developed some 50 years ago. Furthermore, pressures in the ultra high vacuum range, near 10^{-10} torr, have reliably been achieved and measured only during the past decade, largely as a result of the pioneering work done by Alpert[1]. Such low pressures are a prerequisite for many problems in solid state research, in particular thin film and surface studies, which require an environment essentially free of residual gases. It can be shown from the kinetic theory of gases that at a pressure of 10^{-6} torr a monolayer of gas will form on an initially clean surface in a second. Thus, even in a system capable of producing 10^{-10} torr the time for making experiments with partially clean surfaces is limited to a few hours.

In the following, the basic features and construction of typical glass systems will be briefly reviewed; a compact, high speed metal system will be described; and finally, a comparison will be made between the two types of systems.

II. GLASS SYSTEMS

Many ultra high vacuum systems made of glass have been described in the literature. Alpert[1] obtained pressures in the 10^{-10} torr range in a small glass system, cut off from the diffusion pumps by a metal valve, using the pumping action of the ionization gauge. Similar pressures have been attained in larger dynamic systems, isolated from the diffusion pumps by two cold traps in series. A system of this type has been described by Schlier and Farnsworth[2] who studied clean surfaces of germanium and silicon.

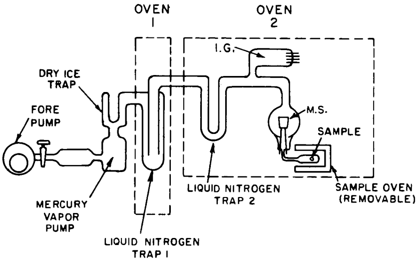
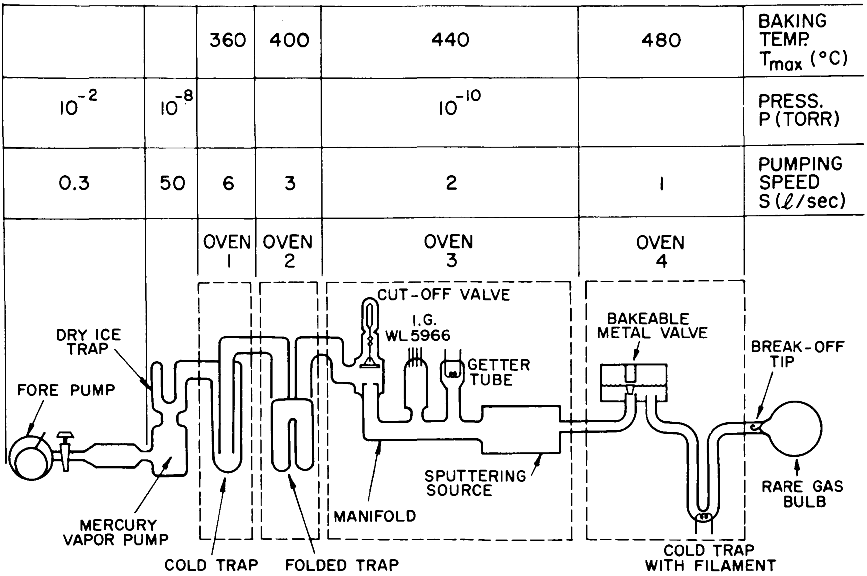


Figure 1

Diagram of glass system used for the determination of residual gases.

This author has used dynamic, multiple trap systems to determine the partial pressures of residual gases with a small mass spectrometer[3] down to the 10^{-11} torr level, and to study surfaces cleaned by ion bombardment[4]. The first of these systems is shown in diagrammatic form in Fig. 1. It consists of the customary mechanical forepump, a ballast volume, a mercury diffusion pump (nominal speed: $50 \ell/$sec), a dry ice trap to prevent the Hg vapor from diffusing back, two liquid nitrogen traps in series, and the miniature mass spectrometer used to determine the gases contained in the sample. As indicated in Fig. 1, three separate ovens are employed to process the system. Oven 1 bakes out the first liquid nitrogen trap. Oven 2 covers the remainder of the high vacuum system, and the small, removable sample oven heats the quartz tube containing the sample. In operation, the system is first evacuated and baked for several hours by ovens 1 and 2, at temperatures of about 350°C. and 400°C. respectively. Next, oven 1 is removed and trap 1 cooled with liquid nitrogen. Subsequently, oven 2 is removed, and liquid nitrogen placed on trap 2. By this procedure, pressures in the 10^{-10} torr range are usually reached after a few days. Finally, the sample alone is heated by the sample oven to the temperature required to remove the occluded gases.



		360	400	440	480	BAKING TEMP. T_{max} (°C)
10^{-2}	10^{-8}			10^{-10}		PRESS. P (TORR)
0.3	50	6	3	2	1	PUMPING SPEED S (ℓ/sec)
		OVEN 1	OVEN 2	OVEN 3	OVEN 4	

Figure 2
Diagram of glass system employed for the study of surfaces.

The more complex system employed to study surfaces is shown in Fig. 2. In this version, a glass cut-off valve, a getter tube, and a gas-handling system are added to the components already discussed. Furthermore, four separate ovens are used to bake the various sections of the system. The baking temperatures indicated in the top line above the diagram (Fig. 2) are adjusted so that the gases evolved are driven towards the pump. The second line shows typical pressures obtained, and the third line estimated pumping speeds for different parts of this system. It is clear from these figures that the large pumping speed existing at the throat of the Hg diffusion pump is seriously reduced by the various traps and the cut-off valve. Another serious disadvantage of this or any glass system is that during the glassblowing operation some of the boron contained in the glass will transfer to the sample. Thus, recent work by Allen[5] has shown that really clean silicon surfaces cannot be obtained in pyrex systems.

III. METAL SYSTEMS

While demountable metal systems or components have been used for many years, they usually employed rubber gaskets and could therefore not be baked. A fully bakeable system using metal gaskets and conventional diffusion pumps has been described by Mark and Dreyer.[6]

The oil-free, all-metal vacuum system used for the evaporation of superconducting films as described by Caswell[7] is different; it uses a water aspirator and a liquid He finger instead of a forepump, while two ion-getter pumps and a second liquid He finger replace the conventional diffusion pump. In this fashion, Caswell has carried out evaporations at pressures below 2 x 10^{-9} torr, free of hydrocarbon contamination.

The system to be discussed in some detail below follows the general approach chosen by Caswell, but uses a simplified design that combines very large pumping speeds with a low consumption of liquid helium.

A. DESIGN AND CONSTRUCTION

The design of the system was based on the following major considerations:

1. To avoid completely oil contamination, gas sorption by "molecular sieve" material at liquid nitrogen temperature replaces the customary forepump, and an ion-getter pump is used instead of a diffusion pump. Since an ion-getter pump need not be isolated by traps from the system, its full pumping speed is available in the work space.
2. Stainless steel was chosen for the vacuum envelope since it is nonmagnetic, can be readily fabricated by arc-welding or brazing, and can be baked at elevated temperatures for degassing. Glass is used only for the ionization gauge stem and the mass spectrometer envelope. The demountable flanges employ metal gaskets, either gold wires or copper washers.
3. To attain an ultimate vacuum of 10^{-10} torr or better, a liquid helium trap (nominal pumping speed for $N_2 \sim 700$ liters/sec) is used. It forms the focal point of the design.

Fig. 3 shows in diagrammatic form the complete ultra high vacuum system, while Fig. 4 shows photographs of the finished structure. In the following, the design and construction of the individual components will be discussed in detail.

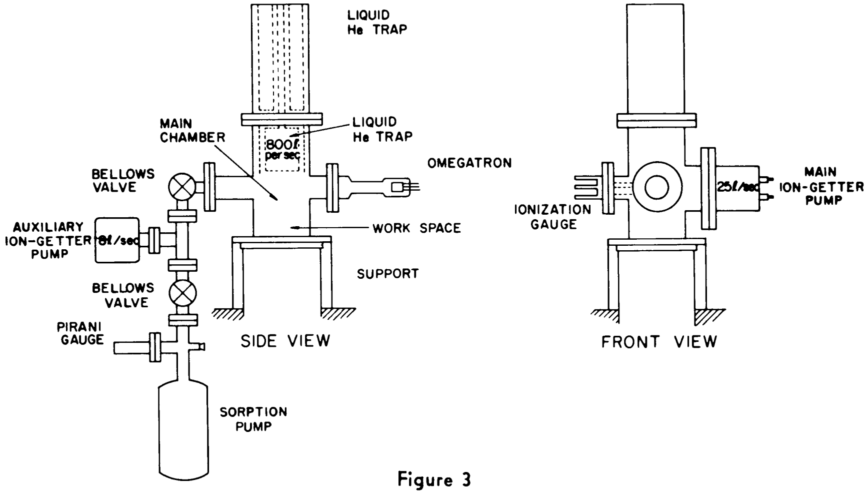


Figure 3
Diagram of metal ultra high vacuum system.

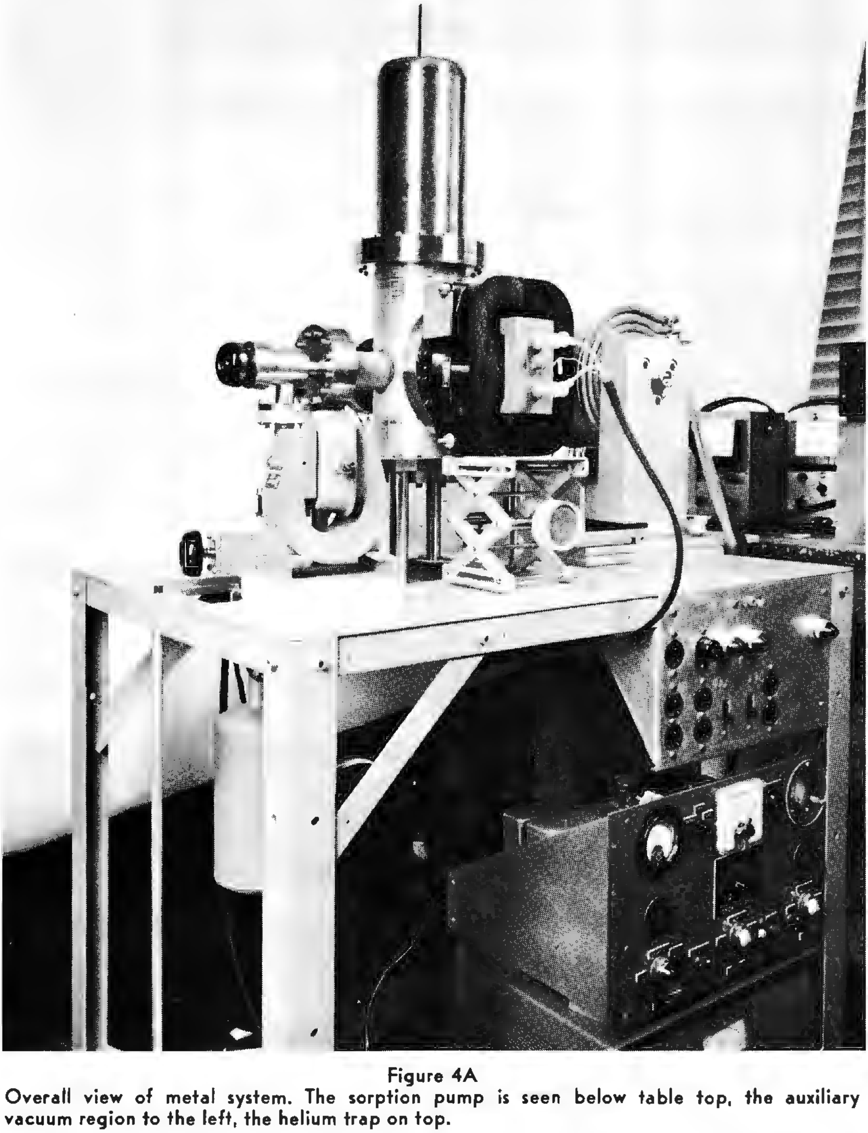


Figure 4A
Overall view of metal system. The sorption pump is seen below table top, the auxiliary vacuum region to the left, the helium trap on top.

The pumping speed to be obtained by the liquid He trap constitutes the starting point for the design, since it fixes the dimensions of the trap and, thereby, of the entire vacuum system. It can be shown that an area A, kept at liquid helium temperature, has a pumping speed for N_2

$$\dot{V}\ (N_2) = 11.9\ A\ \text{liters/sec.}$$

For H_2 at room temperature,

$$\dot{V}\ (H_2) = 44.6\ A\ \text{liters/sec.}$$

Figure 4B
Close-up of system, showing main valve to the right, ionization gauge to the left, and the omegatron between the poles of the main magnet.

Figure 4C
Close-up of system, showing details of the omegatron mass spectrometer.

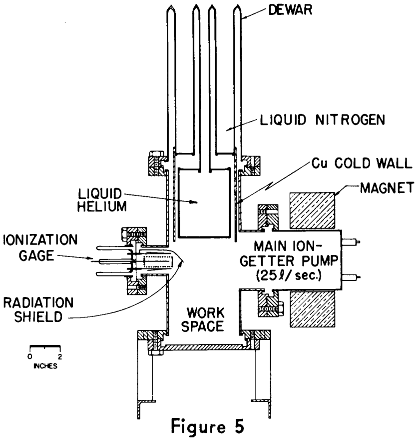


Figure 5
Scale drawing of liquid helium trap and of main vacuum chamber.

It is obvious that cold surface A should be made as large as is compatible with other requirements. To conserve liquid He, the cold trap must be designed to minimize radiation and conduction losses. To this end, the liquid He trap is surrounded on all sides except one by walls at liquid nitrogen temperature, and is supported from a thin S.S. tube of minimum thermal conductivity. To keep the entire container near liquid He temperature, it should be of high thermal conductivity. The design and construction evolved from these requirements is shown in Fig. 5. The container is fashioned from a standard 600 ml stainless steel beaker, to which a stainless steel top is welded. This assembly is then plated with a 0.015″ layer of silver. In addition, all interior surfaces of the assembled liquid He trap, including the cold wall, are coated with a 0.0005″ layer of silver, to reduce radiation losses. The bottom of the liquid He container has the following theoretical maximum pumping speeds: for N_2, $\dot{V}\ (N_2) = 11.8 \cdot 58.5 = 696$ liters/sec; and for H_2, $\dot{V}\ (H_2) = 44.6 \cdot 58.5 = 2610$ liters/sec. It will be shown below how these theoretical pumping speeds agree with the values inferred from experimental data.

The design of the main vacuum chamber combines maximum pumping speed available in the work space with the simplest geometry possible. As is evident from Fig. 5, the 5″ O.D. vertical tube is a continuation of the outer dimension of the He trap, the large bottom flange is available for mounting the work desired, and four short side tubes provide connections for the fore vacuum line, the ionization gauge, the mass spectrometer, and the ion-getter pump. For the ion-getter pump connections, 4″ O.D. tubing was employed whose conductance matches that of the pump envelope, in order to take full advantage of the pumping speed available. All welds were made by internal argon arc-welding. The total volume of the system amounts to about 5 liters.

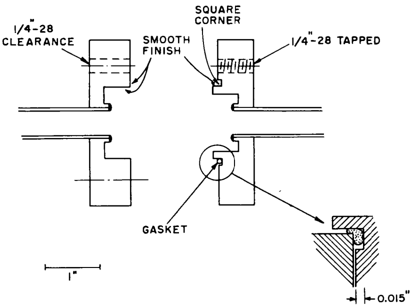


Figure 6
Design details of flanges for 2″ O.D. tube.

The flange construction, shown in Fig. 6 for a 2″ tube, is based on a design by Mark and Dreyer[6] and uses gold wire gaskets. As indicated in Fig. 6 (insert), the initially round wire is deformed into an L-shaped cross-section. The 0.015″ recess was meant to limit the compression of a 0.030″ wire to half its original thickness. However, it was soon established that, with the bolts pulled tight, the flanges are deformed so that a 0.030″ wire will not flatten sufficiently to provide a leak-proof seal. Therefore, wires of 0.040″

to 0.060″ diameter have been used in actual practice. To avoid deformation, any future designs will employ the double gasket principle where an outer gasket is used to keep the flange surfaces parallel to each other. For the forevacuum system, commercial flanges with copper gaskets were used. After all major flanges had been assembled, the system was thoroughly tested for leaks with a leak detector, and bolts tightened where necessary.

Ion-getter pumps are commercially available under various trade names. A pump with an air speed of 25 liters/sec. was chosen which is mounted in an envelope of high conductance, and operates very stably because of its three-electrode construction. The profile of its mounting flange was modified to make it conform to the flange system described above.

The mass spectrometer to be used for the analysis of residual gases should have high detection sensitivity, be small and of open electrode construction, and be readily degassed. These requirements are met by the so-called "omegatron", an instrument first developed by Hipple and Thomas[8] in 1949, and recently modified for stable operation by Klopfer[9]. If properly adjusted, this compact instrument can detect partial pressures as low as 10^{-10} to 10^{-11} torr, with a resolving power of about 45. Unfortunately, it does require a relatively massive magnet that can produce a field which is highly homogeneous over a volume of about 100 cm^3, and mechanical provisions must be made to align precisely the magnetic field with the tube axis. In spite of these drawbacks, the omegatron is better suited for residual gas studies than any other instrument. Omegatrons of Klopfer's design are commercially available[10]. A tube was obtained and was joined to a flange via a S.S.-glass seal[11]. The associated equipment required to operate an omegatron includes an r.f. oscillator, a magnet with stabilized supply, a simple D.C. voltage supply, a filament supply, and a sensitive electrometer.

The ion gauge used to measure total pressures is shown in Fig. 7. The design is based on the Bayard-Alpert type[12], but modified to bring out the collector wire coaxially with the other leads. Thus the gauge can be mounted directly, via a S.S.-glass seal, on a flange and placed inside the main vacuum chamber. This type of mounting, sometimes referred to as "nude", insures that the gauge will measure the pressure in the system rather than in its own envelope. The collector wire is made of 0.004″ tungsten which is probably the best compromise between mechanical stability and a low x-ray background.

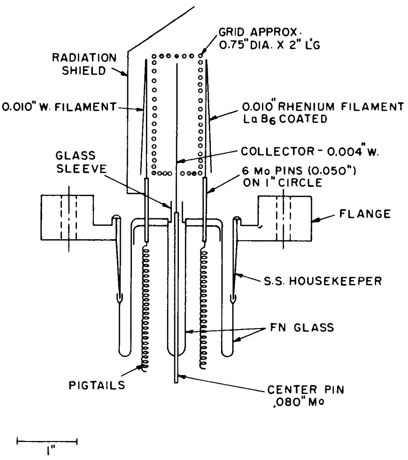


Figure 7
Scale drawing of "nude" ionization gauge.

The radiation shield shown in Fig. 7, serves to protect the liquid He container from direct radiation from the hot filament.

Since ion-getter pumps remove the gas molecules completely from the system, no conventional forepump is required. However, a forevacuum of about 10^{-2}

torr is needed to start the ion-getter pump. This is readily achieved with the help of zeolite ("molecular sieve") cooled to liquid nitrogen temperature. Pumps of this type are commercially available[13], have a physical volume of about two liters and are filled with two quarts of "Molecular Sieve"[14]. Once the ion-getter pump has been started, the forevacuum system is valved off by the lower bellows valve shown in Fig. 3. A Pirani gauge is used to indicate the fore pressure in the micron (10^{-3} torr) range.

The auxiliary small ion-getter pump located between the two bellows valves serves to exhaust the main system during bake-out to a pressure near 10^{-5} torr. Bakes made at sorption pump pressures (between 10^{-3} and 10^{-2} torr) have been quite successful, but it was felt that lower pressures would be beneficial. The auxiliary pump can be run from the same supply as the main ion-getter pump.

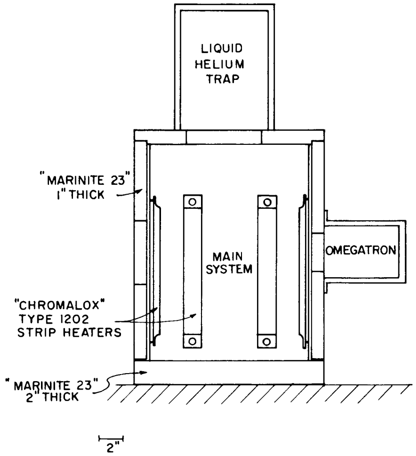


Figure 8
Cross sectional view of baking ovens.

To degas the entire ultra high vacuum sytem up to the main valve, a light-weight oven was designed and constructed which can be handled by a single man, without recourse to clumsy frameworks and counterweights. The oven consists of four parts: two rectangular half-sections that cover most of the main system, a cylindrical top for the helium trap, and a smaller cylindrical side-oven for the mass spectrometer. The larger of the rectangular half-sections contains six, the smaller four Type 1202 "Chromalox" strip heaters (115V, 250W). In each section, the heaters are fed alternately by two separate circuits, so that the ovens can, if desired, be heated by half of the units. The ovens were made of 1″ thick "Marinite-23", a light-weight insulating material[15] of fair mechanical strength. The cylindrical ovens were made of stainless steel cylinders. The larger one, 7″ dia. x 9″ high, was wound with three "Briskeat" electrical heating tapes, 8′ long x ½″ wide. The smaller one, 4″ dia. x 6″ high, was wound with a single 8′ length of tape. Fig. 8 is a cross-sectional drawing of the assembled ovens.

In addition, an oven was constructed, 5″ dia. x 11½″ high, wound with two lengths of 8′ tape, which is used to reactivate, whenever necessary, the molecular sieve material in the sorption pump. This bake is done in air, at about 350°C., and removes mainly water and any hydrocarbons from the material.

B. PROCEDURE

For a typical pumpdown, the bellows valve is first closed and the sorption pump cooled with liquid nitrogen. A fore-pressure of less than 10^{-2} torr is usually reached within 30 minutes. At this point, the valve is opened and the main system pumped until the pressure has dropped once again to 10^{-2} torr or less. Now the valve is closed, the ion-getter pump is turned on, and its behavior closely watched. If the pressure in the main system does not drop within about one minute, the pump is briefly turned off, in order to keep it from overheating, and then the pump is turned on again. Depending on the past history of the pump and the system, this cycle may have to be repeated several times. Once the pump has taken hold, the pressure will drop to the 10^{-8} torr range within one hour. If the system is reasonably clean, it will go below 10^{-8} torr within the next day, without baking or cooling.

To bake out the system, the following steps are taken: the sorption pump is precooled; the ion-getter pump is turned off and its magnet is removed; the ion gauge is turned off and its leads are removed; all omegatron leads are disconnected, the vibrating reed preamplifier removed, and the magnet moved out of the way. Once the oven sections are set in place and the forevacuum is at a pressure of a few microns, the valve is opened and baking begins. Temperature of the two large oven sections is maintained near 350°C. to about ± 10°C. by a bimetallic theremoswitch. The two small ovens are kept at about 380°C. by Variac control. A typical bake-out may last from one to fifteen hours. To bake the system at lower pressures, the small ion-getter pump is used instead of the sorption pump.

After the ovens are turned off and removed, the ion pump is started up, the ionization gauge degassed by electron bombardment, and the metal parts of the omegatron heated to about 800°C. by r.f. bombardment. If necessary, the entire system may be given another short bake at this time.

In view of the high cost of liquid He, it is important to effect the transfer from the dewar to the trap with minimum losses. The outer trap, as well as the liquid He trap, are cooled with liquid N_2. When the inner trap has reached temperature equilibrium at 77°K., He gas is blown in to remove the liquid N_2 completely. To keep the transfer tube from plugging up with frozen O_2 or N_2, it is flushed with He gas. Now liquid He is transferred to the inner trap until it is full, as indicated by dense clouds forming above the trap. It was found that a full charge (600 ml) of liquid He lasts about four hours, provided the cold bottom surfaces sees only walls at room temperature. When a filament, located nearby, is at emitting temperature (about 2400°K.), the liquid He charge will last not more than 2½ hours.

For initial adjustment and subsequent operation of the omegatron, the scheme outlined by Klopfer was followed. Briefly, this consists of activating the oxide-coated cathode, of aligning the magnetic field and of making a series of voltage adjustments to obtain maximum ion current for specific masses. The omegatron equation applied to this particular instrument yields a resonant frequency

$$f = 1533B/M \tag{1}$$

where

B = magnetic field, in gauss
M = atomic mass, in a.m.u.

The resolving power $M/\triangle M$ is given by

$$M/\triangle M = 3.6 \cdot 10^{-5} \frac{B^2}{V_{rf} \cdot M} \tag{2}$$

It is apparent from Eq. (2) that for optimum resolving power the magnetic field B should be maximized and the r.f. voltage minimized. It was found that the magnet can be operated at 5000 gauss without serious overheating. The value of V_{rf} is adjusted to yield adequate resolving power and, at the same time, good ion beam intensities. The best compromise value is $V_{rf} = 0.08$ volts which permits to separate masses 44 and 45 at near maximum beam intensities. For masses 2, 3, and 4, where resolving power is of no concern, r.f. voltages as high as 0.8 V were employed. It was found, in agreement with Klopfer's statement, that the omegatron did not operate satisfactorily until its electrode structure had been thoroughly degassed by baking and r.f. heating.

In order to estimate total pressures near 10^{-10} torr with the ionization gauge, it is necessary to evaluate the ion current due to the x-ray effect, as discussed by Alpert and Buritz[16] and more recently by Lange[17]. This is done by plotting log p as a function of log E_g, where E_g is the ionizing voltage. It is found that the x-ray contribution amounts to about 4 x 10^{-11} torr at $E_g = 100$ v, and 2.5 x 10^{-11} torr at $E_g = 75$ v. In view of a number of uncertainties, all pressures between 10^{-9} and 10^{-10} torr, quoted in Tables I and II, are only estimates and constitute upper limits.

C. RESULTS

Table I summarizes processing details (baking and r.f. treatments), the application of coolants, and the ultimate total pressures achieved, as indicated on the ion gauge. To convert from indicated pressure p_I to true pressure p_T (sometimes called "N_2 equivalent pressure") we must know the composition of the residual gases, determined by the mass spectrometer, and their individual ionization cross sections. Details of the method employed go beyond the scope of this paper. It is seen from Table I that baking the system for a total of about 52 hours at temperatures up to 400°C., reduces the total pressure by one order of magnitude, to about 6 x 10^{-9} torr (no coolant on the traps). The first five bakes were done at about 10^{-2} torr, the ultimate pressure of the sorption pump. For the sixth bake, a mechanical forepump was connected, via a liquid N_2 trap, to the sorption pump, which lowered the pressure roughly by one order of magnitude. For the last bake, the auxiliary ion-getter pump was installed and employed to reduce the system pressure to between 10^{-4} and 10^{-5} torr. The ultimate pressures shown in Table I indicate that baking at lower pressures does result in slight improvements. The application of liquid N_2 cuts the pressure before the first bake in half, but does not help much once the system has been baked. When the inner trap is filled with liquid He, the pressure is reduced approximately another two orders of magnitude. It should be noted that the ultimate vacuum achieved with liquid He improves progressively with baking ($p_T = 4.8$ x 10^{-10} torr before first bake, ≤ 1.0 x 10^{-10} torr after 52 hours). These facts, taken together, indicate that a large fraction of the residual gas must be H_2, as will be shown below.

Assuming, for the time being, the residual gas to consist entirely of H_2, we can estimate the effective pumping speed of the liquid He trap by applying the well-known definition[18] of gas flow

$$Q = S\triangle p \tag{3}$$

where
Q = rate of gas flow, in torr-liters/sec.
S = pumping speed, in liters/sec.
$\triangle p$ = pressure differential, in torr

In this case, Q is simply the rate of gas evolution which does not depend on pumping speed, and $\triangle p$ is the residual gas pressure. Thus we may write

$$S_1 p_1 = S_2 p_2 \tag{3a}$$

where subscripts 1 and 2 refer respectively to ion-getter pumping and to liquid He pumping. From the speed quoted by CVC[19] for their "Drivac" pump for H_2 ($S_1(H_2) = 50$ liters/sec.), and the ultimate pressures given in row 7 of Table I, we obtain a liquid He pumping speed $S_2(H_2) = 3000$ liters/sec. This agrees well

TABLE I - PROCESSING OF SYSTEM AND ULTIMATE PRESSURES ACHIEVED

BAKE				RF	COOLANT		TOTAL PRESSURE IN 10^{-10} TORR	
No.	CONDITION	DURATION (HOURS)	T_{max} (°C)		OUTER TRAP	INNER TRAP	INDICATED p_I	TRUE p_T
0a	Sorption pumped	None	25	–	–	–	200	610
b	10^{-2} torr				N_2	N_2	100	340
c					N_2	He	2	4.8
1a	Sorption pumped	4.5	310	–	–	–	90	200
2a	Sorption pumped	4.25	320	√	–	–	70	270
3a	Sorption pumped	4	340	–	–	–	80	290
b					N_2	N_2	95	320
c					N_2	He	0.8	1.8
4a	Sorption pumped (air leak)	24	335	√	–	–	65	260
5a	Sorption pumped	1	380	√	–	–	40	140
6a	Forepump	4	330	–	–	–	27	80
b	10^{-3} torr				N_2	N_2	23	65
c					N_2	He	0.7	1.7
7a	Vacion pumped	6	390	–	–	–	27	70
b	10^{-4} torr				N_2	N_2	22	60
c					N_2	He	≤ 0.4	≤ 1.0

with the value computed above, $\dot{V}(H_2) = 2610$ liters/sec. In fact, the agreement is probably better than is warranted by the quality of the data. For nitrogen gas, the corresponding values are

$$S_2(N_2) = 800 \text{ liters/sec. (experimental)}$$
$$\dot{V}(N_2) = 696 \text{ liters/sec. (computed).}$$

During the course of this study, a total of nearly ninety mass analyses were undertaken. The most significant of these runs have been summarized in Table II, arranged so they can be correlated with the data of Table I. For each component n, the ion current I_n^+ recorded by the mass spectrometer was first divided by the corresponding cross section Q_n, the quotient I_n^+/Q_n being proportional to the partial pressure and yielding mole per cent. With the help of these percentages, the true total pressures p_T were computed, as mentioned above, and finally the absolute partial pressures obtained for each component. This method implies that the total pressure and composition of the residual gas is the same in the mass spectrometer and ionization gauge, which may not always be true.

Aside from H_2, which always is the predominant species, the major constituents found in the residual gas are: He, Ne, CO, CH_2, H_2O, Ar, and CO_2, arranged in descending order of intensity. The presence of H_2 is due to prefiring all S.S.

TABLE II — SUMMARY OF PARTIAL PRESSURES OF RESIDUAL GASES (IN 10^{-10} TORR)

RUN	CONDITION	COOLANT	H_2		He		CH_4		H_2O		Ne		CO		Ar		CO_2		TOTAL PRESSURE P_T	RATIO $\frac{\Sigma I^+_{MS}}{I^+_{IG}}$
			pp	%	pp	%	pp	%	pp	%	pp	%	pp	%	pp	%	pp	%		
0a	Before Bake 1	–	487	79.9	45	7.4	3.0	0.5	2.4	0.4	46	7.6	23	3.8	2.4	0.4	0.2	0.03	610	1.13
0b		N_2	212	62.4	38	11.3	3.4	1.0	2.4	0.7	50	14.8	31	9.2	2.0	0.6	0.3	0.09	340	0.60
0c		He	4.7	97									0.1	3					4.8	0.45
1a	After Bake 1	–	NO RELIABLE RUN AVAILABLE																200	–
2a	After Bake 2	–	222	82.1	19	7.0	1.4	0.5			15	5.4	13	4.7					270	0.40
3a	After Bake 3	–	222	76.6	35	12.0	2.0	0.7			22	7.7	7.5	2.6	0.3	0.12			290	0.34
3b		N_2	255	79.8	38	11.9	1.6	0.5	1.0	0.3	19	5.9	4.5	1.4	0.6	0.2			320	0.25
3c		He	1.5	85									0.3	15					1.8	0.38
4a	After Bake 4	–	123	47.2	58	22.5	2.6	1.0			34	13.2	46	17.5	0.1	0.04			260	0.41
5a	After Bake 5	–	91	65.1	26	18.8	0.7	0.5	0.7	0.5	8.0	5.7	13	9.4					140	0.52
6a	After Bake 6	–	60	74.6	6.1	7.6	0.8	1.0			4.6	5.7	8.7	10.9					80	0.40
6b		N_2	54	82.5	3.8	5.9					3.1	4.7	4.6	7.0					65	0.33
6c		He	1.7	100															1.7	0.18
7a	After Bake 7	–	59	83.8	2.0	2.8	0.4	0.6			2.2	3.2	6.5	9.2	0.2	0.3			70	0.52
7b		N_2	56	93.8	1.7	2.8					1.4	2.4	0.5	0.8					60	0.53
7c		He	$\leq$1.0	100															$\leq$ 1.0	$\geq$.25

TABLE III

COMPARISON OF ULTRA HIGH VACUUM SYSTEMS

CONVENTIONAL GLASS SYSTEM			NOVEL METAL SYSTEM		
	PRESS. P (TORR)	SPEED S(ℓ/sec.)		PRESS. P (TORR)	SPEED S(ℓ/sec.)
Forepump (Mechanical)	10^{-2}	0.3	Sorption Pump	10^{-2}	
(Trap)			(Valve + Small Ion-Getter		
Diffusion Pump (Hg or Oil)	(10^{-8})	50	Pump, Used During Bake-Out)	10^{-7}	8
Dry Ice Trap			Valve, Bakeable		
Liquid N_2 Trap 1		6	Ion-Getter Pump	10^{-9}	25
Liquid N_2 Trap 2		3	Liquid He Trap	$< 10^{-10}$	800
Glass Valve			Work Space	$< 10^{-10}$	800
Getter					
Work Space	2×10^{-10}	2			
Ion Gauge		0.1			
ADVANTAGES					
Fabrication Easy			High Pumping Speed in Work Space Demountable Flanges High Temp. Firing Cleans Component Parts No Servicing Required No Ionization Gauge Needed		
DISADVANTAGES					
Low Pumping Speed in Work Space Bakes Limited to 500°C Hydrocarbon Contamination From Forepump Breakage of Glass Components Forepump Noise and Wear			Fabrication Complex H_2 Firing Leaves H_2 in Walls		

parts in dry H_2 before machining, done in order to remove strain. The rare gases He, Ne, and Ar are atmospheric constituents, left in the system because of the pumps employed. Sorption at liquid N_2 temperature is only partially effective for rare gases[20], while the CVC "Drivac" pump removes them only with speeds between 5 and 8 liters/sec.[19] The absence of hydrocarbons even in the unbaked system is remarkable and points out clearly one of the major advantages of this design. The only exception is CH_4 which seems to be formed in the ion-getter pump[21], but its partial pressure after baking is below 10^{-10} torr. The concentration of CO is abnormally low compared to that found in diffusion-pumped glass systems where CO is usually the major component.

To compare the pressures in the mass spectrometer and the ionization gauge, the total M.S. ion current, $\Sigma\, I^{+}_{MS}$, summed up over all peaks, was compared to the ion gauge current I^{+}_{IG}, both values being quoted per unit electron current I^{-}. The resulting ratio $\Sigma\, I^{+}_{MS}/I^{+}_{IG}$ is given in the last column of Table II and lies, with a few exceptions, between 0.3 and 0.6, the mean value being 0.4. This is reasonable since the active length for ionization is several times longer in the gauge than in the mass spectrometer. The exceptionally high ratio obtained for Run Oa may be due to the fact that the mass spectrometer, not yet degassed, was evolving gas at a rate faster than the ionization gauge. For the last two liquid He runs, the ratio is abnormally low, indicating that after thorough baking the ionization gauge is the prime source of gas. With the trap at 4.2°K., gas evolved in the I.G. is registered there, but condenses on the cold surface before it can reach the M.S.

The results obtained indicate that ion-getter pumping combined with liquid helium pumping yield high pumping speeds. The ultimate vacua recorded—5×10^{-9} at room temperature, $< 1.0 \times 10^{-10}$ at liquid He temperature—are somewhat higher than expected, the predominant constituent being H_2. This suggests that it might have been better not to fire the S.S. parts in dry H_2 before machining; certainly, vacuum firing would have been indicated. If the H_2 partial pressure could be reduced one order of magnitude, the total pressure would drop by a factor of five.

III. COMPARISON OF GLASS AND METAL SYSTEMS

Having discussed separately the constructional and operational details of glass and metal systems, it is now of interest to compare their performances and bring out their respective advantages and disadvantages. The most important points have been summarized in Table III.

While glass systems after proper processing will produce vacua in the 10^{-10} torr region, the pumping speed realized is severely reduced by the cold traps required to protect the working space from the pump vapors. Contamination by hydrocarbon vapors from the mechanical forepump is unavoidable when the system is first pumped down, and can be reduced only by prolonged baking. Baking temperatures are of course limited to below the softening point of the glass employed, and it is therefore impossible to remove all occluded gases from the walls. Around-the-clock attention is required to keep up the refrigerant level in the cold traps, and the noisy mechanical forepump is subject to wear. Complex devices are required to protect the equipment, particularly filaments should power and cooling water fail. A glass system cannot be made demountable and at the same time retain its ultra high vacuum character. Finally, glass components are fragile and apt to fail, often causing extensive damage to expensive filaments. The only true advantage of a glass system lies in its relatively easy fabrication by a skilled glass blower, allowing its shape to be changed quite readily.

Metal system, on the other hand, are truly demountable. A sorption pump, free from any hydrocarbon contamination, produces the forevacuum required by the ion-getter pump, and is valved off immediately after the initial pumpdown. The full pumping speed of the ion-getter pump is available since there are no in-line cold traps to separate it from the working space. The only cold trap used is the liquid helium trap which is filled only when vacua below 10^{-10} torr and very high pumping speeds are required. Component parts are made of stainless steel which is prefired in dry hydrogen, at 1065°C., thereby removing all occluded gases except H_2. To remove the residual H_2, it would be preferable to vacuum-fire all S.S. parts. This system contains no moving parts, requires no cooling water, and is not ruined by a power failure. Its major disadvantage lies in the fact that fabrication is complex and requires special facilities and advanced knowledge in arc-welding and brazing.

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RELEASE OF ALKALIES AND FLUORINE FROM GLASSES AND THEIR INFLUENCE ON GLASS SEALING

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1. INTRODUCTION

The release of gases by heat plays an increasingly important role in electronic tubes and T.V. tubes; extensive studies were done and are continuously undertaken to understand the factors influencing release of any kind of gas. Only limited attention was paid in the past to the heat effects on glass which affect the glass sealing characteristics. When a flame makes a contact with glass, the flame becomes colored, *e.g.*, yellow from sodium in a glass or purple from potash or red from lime. This flame coloring is due to volatilization of glass components resulting in alterations of glass composition at the flame contact spot. In alkalies release, the net result is increased silicon content in silicate glasses. When flourine is released two things can happen to the glass: one, the silicon content will be higher, or, two, fluorine can take some silicon with it in a form of a compound with very high vapor pressure known as silicon tetra fluoride (SiF_4) or silicon hexafluoride (SiF_6). In the latter case the silicon content can be lower or equal to the original glass composition before heat was applied. We examined the alkalies and fluorine release to find out which of these conditions are actually prevailing. This problem is, of course, of considerable practical importance, because it may offer a possibility of designing glasses which might remain unchanged by direct flame, and the glasses could be then sealed without any composition stresses. This could be achieved if the process of alkalies and fluorine release could be controlled and balanced, so that the siliceous excess remaining in glass after alkalies left it could be removed by fluorine volatilizing out as silicon fluorides. For a glassblower this balance could mean mechanically strong seals and chemically homogeneous sealing edges.

2. THEORETICAL CONSIDERATIONS

The statements expressed in the introduction should be clarified in more detail so that this interesting problem can be better understood. A simplified form of what is happening to the glass during direct flame heating is shown in Fig. 1.

The left side of this diagram shows ordered state of glass arrangement before flame contact and the right side shows rearrangements of structures after flame heating. In upper half of the same diagram glass without fluorine is shown and in lower half glass contains small amount of fluorine. For the sake of clarity equal amounts of sodium and silicon are present in these hypothetical glasses even though the commercial products contain as much as five times up to twenty times more silicon than sodium. Soon after the flame touches the glass, the surface sodium will vaporize and color the flame yellow. Silicon will remain and our arbitrary ratio of 1:1 of sodium to silicon will be changed to 1:2. The glass layer next to the glass/air boundary will be affected also by this change. The released sodium makes openings in the surface layer and the sodium in the second layer will move slowly into the new position between these openings and its original spot. The force which helps the deep sodium to move is called concentration gradient (= difference of sodium concentration between second glass layer and

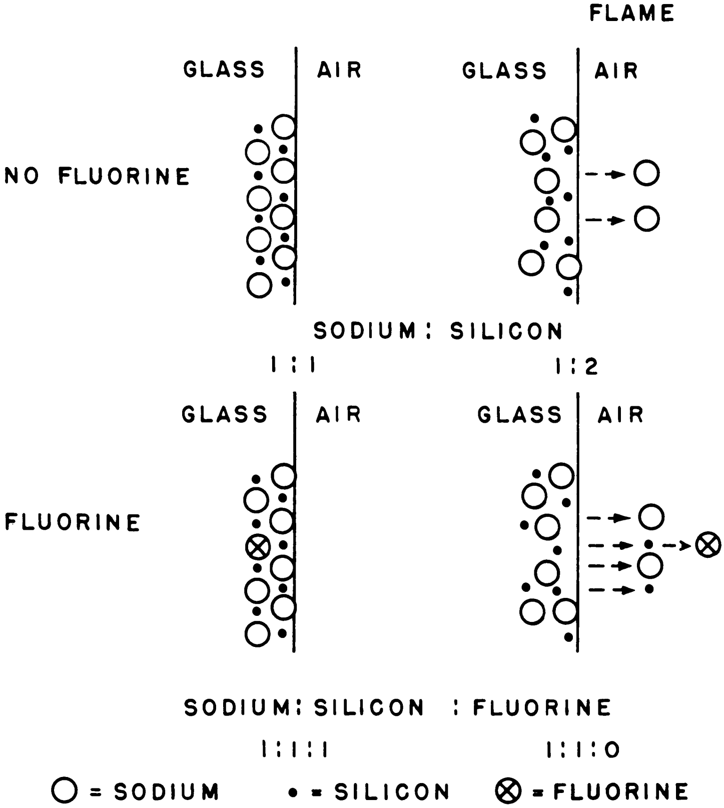

Figure 1
Schematic Diagrams of Sodium and Fluorine Volatilization by Direct Flame.

the first surface which was flamed). The motion or migration of sodium ions is also known under the name of diffusion. Similarly the third and fourth consecutive layers will be influenced and sodium will start diffusing through the heated glass. The sodium leaving the glass surface can diffuse into air or flame quite easily, because only gas molecules are in its way and they like to move around to make room for the newcomer. On the other hand, sodium moving within glass has more resistance on its way and has to push some silicons around. Furthermore, the siliceous layer is more viscous, and the temperatures are lower within the glass than in the flame contact area. The net result of all these considerations is the fact that internal sodium never can replenish and equalize the original surface sodium which was released. In the next parts, quantitative and visual proofs will be offered to support these theoretical considerations.

Another interesting case to consider is glass with small amounts of fluorine and its behavior in flame heating. The sodium will volatilize similarly as discussed above. Furthermore, measurable quantities of fluorine are also released. The fluorine can be released in several forms (hydrogen fluoride, alkalies fluoride, silicon tetrafluoride, silicon hexafluoride) and two of these contain silicon and have very high vapor pressure. The diagram in Fig. 1 shows a situation when fluorine left the glass surface and took with it some silicon. In this hypothetical case, the final glass composition is shown identically as far as ratio of sodium to silicon is concerned and differs only in loss of fluorine. In real practice it is not easy to obtain this ideal condition. At lower temperatures of the order of annealing point, fluorine is driven out mostly as hydrogen and alkali fluoride. At softening point and sealing temperatures, fluorine can leave as compound with silicon. The theoretically ideal conditions for sealing can be arrived at by perfect control of temperatures and times. Or, in other words, the rates of alkali release and fluorine release have to be adjusted so that the final glass product will be balanced in content of sodium and silicon comparable to the original glass before flame was applied.

In the following sections of this paper, the real conditions of flamed glass surfaces will be examined after brief description of the experimental techniques useful for this type of investigation.

3. EXPERIMENTAL

An unique technique-immersion interferometry was developed for examination of surface and interfaces of transparent solids. Alkalies and fluorine release was studied by vacuum, high temperature systems.

3.1 *Immersion Interferometry*

As the name suggests, the sample is immersed, and the light passing through this sample is made to interfere between two mirrors. One of these mirrors is placed above the immersed sample and one below. The collimated light is reflected back and forth by both mirrors. In some positions the light beams will reinforce each other and in this case a light line or band can be seen in the microscope. In other positions the two beams will cancel each other and then a dark cut off line or band is viewed by an attached microscope. The net result is a system of lines called fringes. These fringes connect points of the sample assembly with identical refractive indices. Practically, this means that straight line fringes show good homogeneity, and any deflection to one side or the other from the straight line is interpreted and calculated in terms of refractive index difference by a simple equation:

$$\triangle n = \tfrac{1}{2} \lambda \frac{A}{t}$$

where $\triangle n$ = refractive index change

λ = wave length of the monochromatic light (*e.g.* 5461 A.U.* for mercury green light)

t = measured thickness of the sample

A = fringe displacement

The importance of this technique lies in the fact that it allows us to very precisely determine refractive indices from point to point, and they in turn are related to the composition changes. The precision is as high as $\pm 1.0 \times 10^{-5}$ and even this can be exceeded by simple improvement of the described technique.

The actual experimental arrangement of the optical system is shown in Fig. 2. Light from a mercury vapor lamp source passes through a condenser,

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*A.U. symbolizes Angstrom Units.

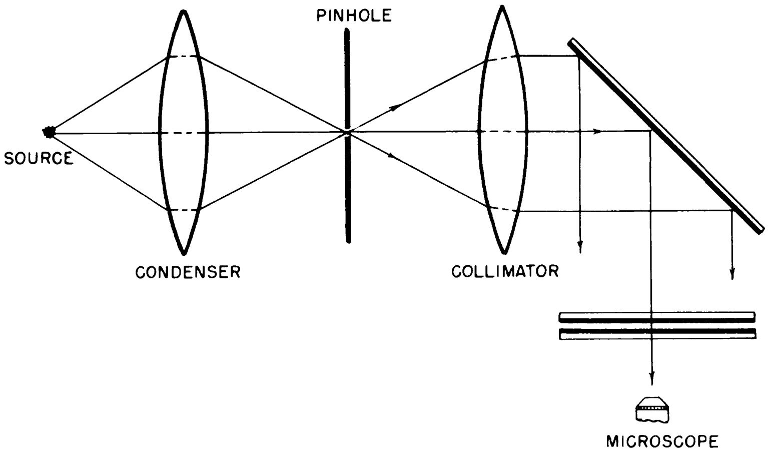


Figure 2
Immersion Interferometry Optical System

then through a filter for 5461 A.U. line to a pinhole. The emerging beam is collimated to a mirror, reflected to the interferometric cell and viewed by microscope. The interferometric cell is shown in Fig. 3. The thin, transparent sample (1) is immersed in a liquid (2) of the same refractive index, both being in the space between the two optical flats with reflecting films. (3) The sample sandwich is surrounded by a heating chamber with a resistance wire (4) enclosed in an airtight space. Temperature of the liquid is measured by the thermocouple. (6) Three screws with fine threads (7) provide sensitive positioning of the mirrors.

3.2 *Instrument for Alkalies Release*

Release of alkalies was examined by an instrument shown in Fig. 4. A glass specimen in a form of jar or vial (1) was placed in a refractory shell located in a furnace. (12) One thermocouple registered the temperature of the specimen (3) and one the temperature of the target plate. (4) Target plate (2) was water cooled by the copper tube (6, 8) to temperature of 350°F. (177°C.) The whole furnace and sample assembly was placed in a metal vacuum chamber equipped with appropriate power, thermocouple, water inlets, etc., and maintained at 0.1 micron Hg. pressure. During heating alkalies release from inner surfaces were collected on the target plate. After completion of run at any specific temperature and time, the collected alkalies were determined by flame photometry in micrograms (10^{-6} gms.) quantities.

3.3 *Equipment for Fluorine Release*

Fluorine release was studied by another instrument shown in Fig. 5. This equipment consists essentially of a tube furnace, sample tube, liquid nitrogen cold trap, Phillips gage, vacuum pumps and thermocouples. A weighed amount of crushed glass of determined surface area was placed in the sample tube and the whole system evacuated to 0.1 microns Hg. pressure. The furnace was turned on and the temperature measured by a thermocouple located inside of the sample tube. The gases evolved were collected in liquid nitrogen cold traps and analyzed by the spectrophotometric methods for fluorine.

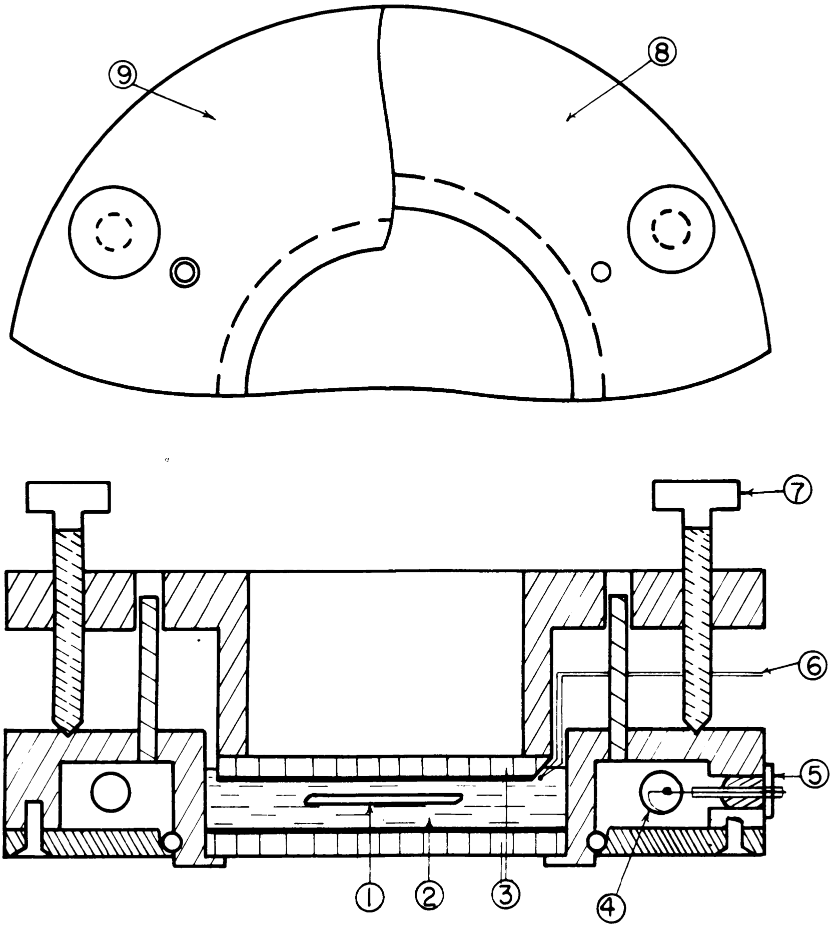


Figure 3
Interferometer Cell

4. RESULTS AND DISCUSSION

4.1 *Interferometry of Flamed Glasses Surface*

First a simple interferogram will be examined to illustrate the type of information interferometry can offer us. Fig. 6 is an immersion interferogram of a glass sample showing a series of inhomogeneities in form of bands. The straight region marked "S" indicates the uniform, good region of this particular sample. The fringe deflections to the left (← and + indicate refractive index increase), deflections to the right are index decreases. Glass surface very lightly touched by flame for short duration is shown in Fig. 7. The flame edge is marked by "F" and indicates uniform deflection of all fringes in the direction of decreasing refractive index. Increase of silicon content caused this type of deflection. The

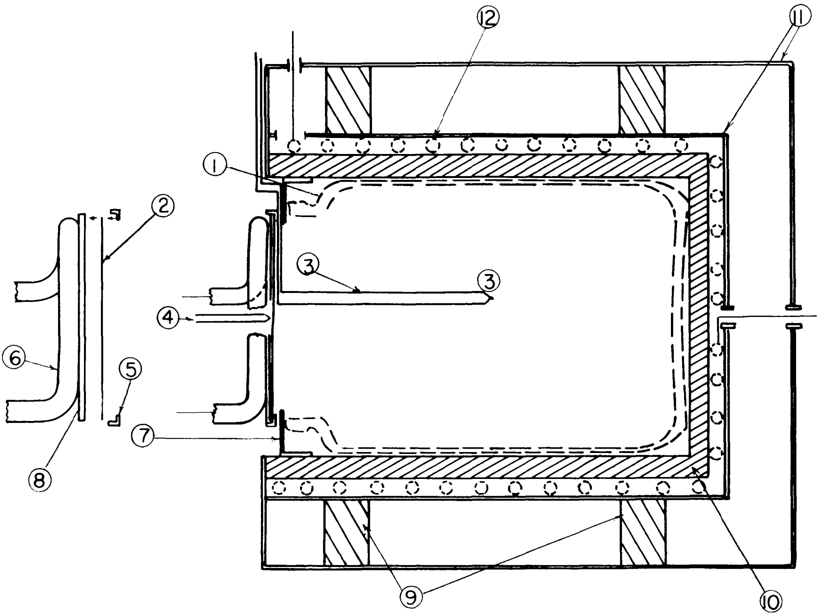


Figure 4
Instrument for Alkalies Release Investigations

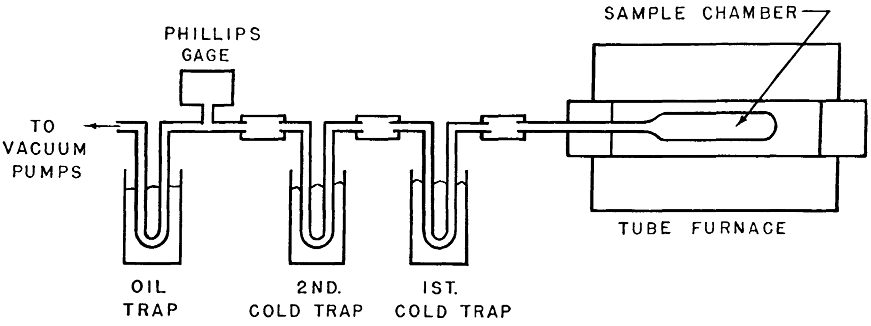


Figure 5
Schematic Diagram of Equipment for Fluorine Release

actual condition is in good agreement with the above described theoretical expectation as shown in diagrams of Fig. 1. Inside of the glass there are several streaks of inhomogeneities, but these are of mild type and consequently the glass quality can be considered very good.

Glass surface contacted by a harder flame is shown in Fig. 8. The deflections are of much higher order in the direction of siliceous layer on the top of the interferogram, amounting to complete fringe shift, marked "S". Boundary of the "Na" region shows the pockets of migrated alkalies to the surface. This case proves

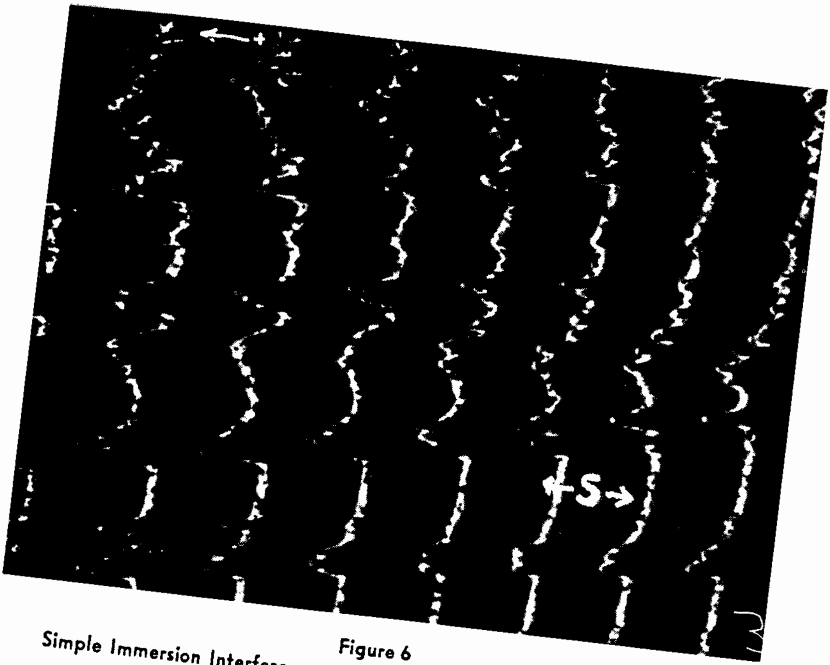


Figure 6
Simple Immersion Interferogram Showing Several Small Inhomogeneities

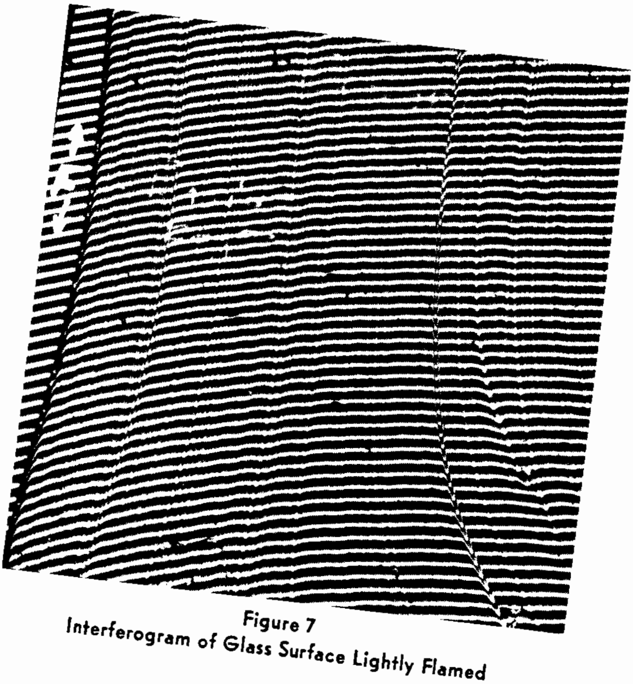


Figure 7
Interferogram of Glass Surface Lightly Flamed

Figure 8
Interferogram of Glass Surface Heated by Hard Flame

also the previous discussion, especially the part where the internal alkalies start to move to take the positions of alkalies removed. The homogeneity of the glass is excellent inside, and is of optical quality.

The extreme case of hard flame application for a long time is shown in Fig. 9. This is an interferogram of an experimental sample prepared to prove that the alkalies release can be carried out to an extreme. The net result is devitrification of this particular glass surface which is shown by discontinuities in fringes at the region marked "D". Here again it can be noted that the theoretical considerations are on a solid ground, namely the siliceous layer is continuously increasing up to 100% of concentration. At this stage the cementing parts of glass building blocks left the surface, with a net result of partially (only in the direction to inside) bonded small crystallites.

Now we are going to examine glass surfaces with overheated (hot spot) regions and lightly heated regions in one sample. Interferograms of this case is shown in the next figure, Figure 10. The surface has highly siliceous streak. Inside layers have alkalies regions sandwiched between siliceous striae. This picture is very interesting because it shows the alkalies diffusion in time pulsing. This is brought up by the temperature distribution in isothermal rings with the hot center around area of flame contact. The heat penetrates in half circles from

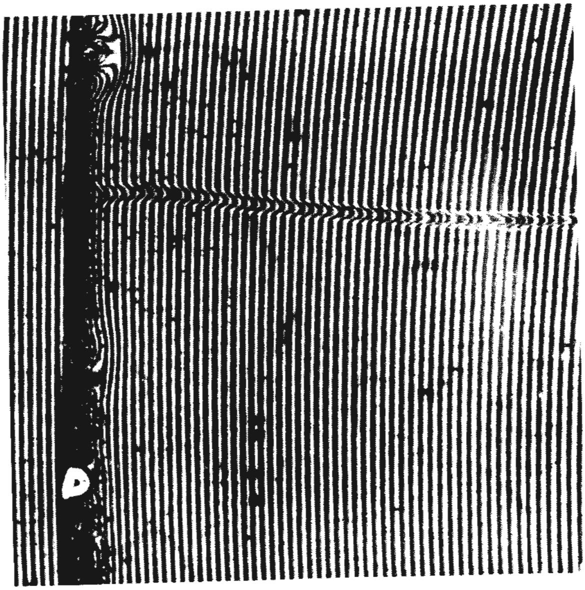


Figure 9
Interferogram of Devitrified Glass Surface by Hard Flame Applied for Extremely Long Times

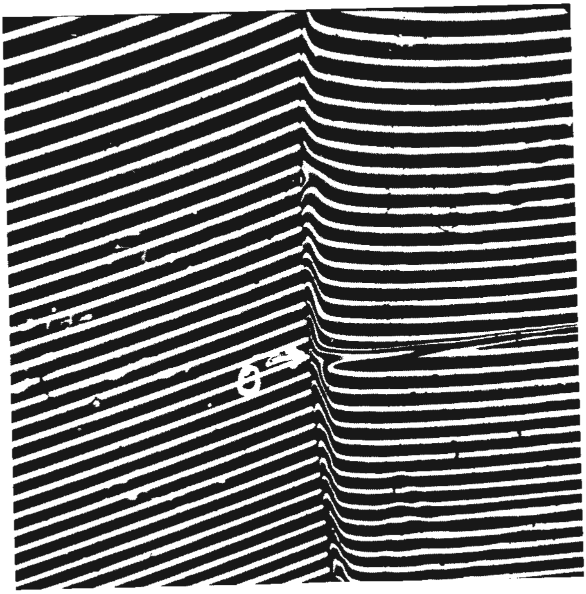


Figure 10
Interferogram of Glass Sample with Overheated and Lightly Flamed Regions

the point source. That is the reason why the alkalies are concentrated in similar half circles. The siliceous striae slow down the migration of alkalies because of the increased viscosity and consequently the alkalies are piling up and stored in this peculiar fashion.

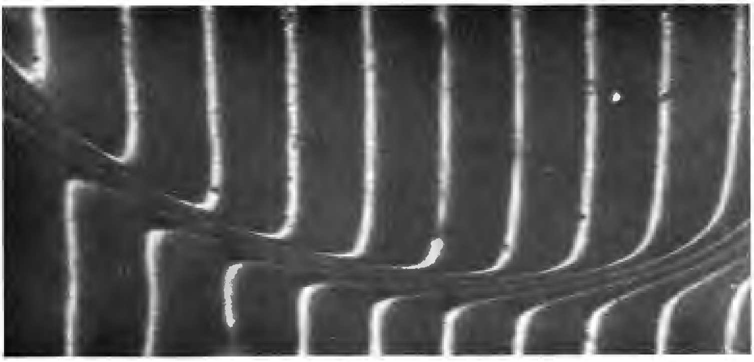
4.2 *Interferometry of Seals*

The above discussion was centered around single glass surfaces heated by direct flame to low and high degrees. Now the sealed surfaces will be shown and the changes occurring at the sealing edge will be examined in detail.

Before going into more complex cases, *an ideal seal* is shown in Fig. 11.

Figure 11
Ideal Seals in Immersion Interferometry:

A. Straight Seal



B. Circular Seal

The set of fringes of one glass are connected without any discontinuities to the fringe system of the other glass. The sealing edge is uniform and the transition is smooth. This type of seal can be obtained by perfect control of temperatures and time of flame application, so that the volatilization and the migration of alkalies are in perfect balance. Before joining both glass surfaces, they had siliceous surface layer and next to it there was a pile of alkalies. During joining the flame was of such order that the migration through the siliceous layer was induced. After the seal joint was made, the migration of alkalies from one glass into the other was in a complete balance.

Figure 12 is an interferogram of *a good seal,* but not ideal. Fringes at the sealing edge have discontinuities of smaller order. The outside edge was heated more than needed. This type of seal is usually made with flame which does not penetrate deep enough into sealing edge and also the blending at the interface is of shorter duration. This seal could become ideal if the flame was more luminous (= less hard, less oxygen), and applied for some two minutes longer.

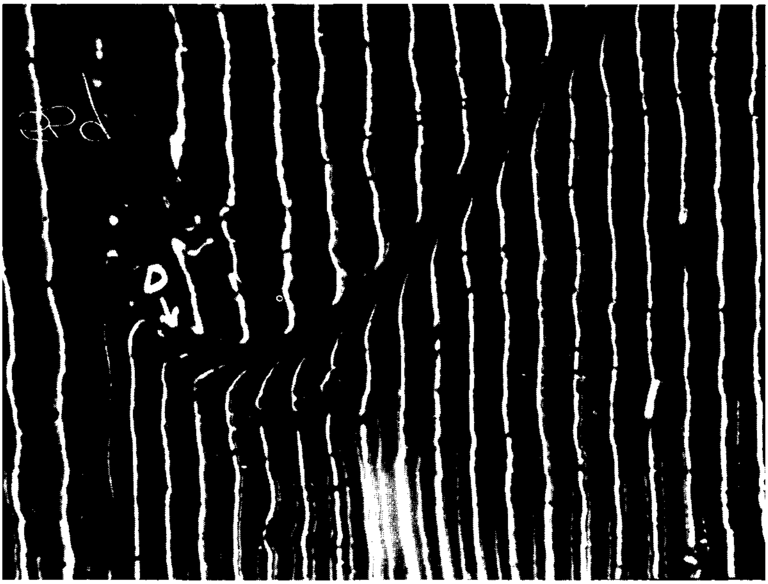


Figure 12
Interferogram of a Good Seal

A *poor seal* is shown in the next figure, Figure 13. The lower part of the seal is overheated, decomposed layer from previous Fig. 10. The fringe deflections are of the two kinds: one corresponding to siliceous striae, and the other to alkalies piles locked in between siliceous barriers. The upper part of the same seal is still good. It can be noticed that the migration of this second part was started but it could not penetrate through the viscous hard skin of mistreated lower part. In this case the heat soaking would have to be done for exended time, and even then the result would be questionable. This example demonstrates clearly the importance of alkali volatilization caused by overheating and its consequences in making poor seals.

A *composite* of several interferograms showing the *entire seal* is shown in the Fig. 14. These glasses contain small amounts of fluorine which helped in making good outside portion of the seal. The fringes are connected. The small deflection at the outside edge is not detrimental. The weak spots of this seal are at the inside edge. More luminous radiant heat can correct this weakness.

4.3 *Alkalies Release*

In the previous paragraph the alkalies release was examined on the individual glass surface and on the seal visually by interferometry. Independent investigations were carried out to obtain further quantitative data about the

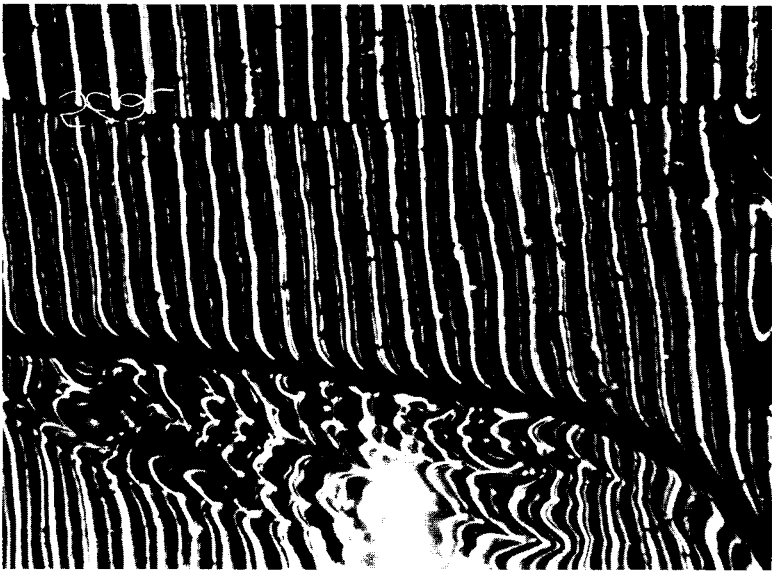


Figure 13
Interferogram of a Poor Seal

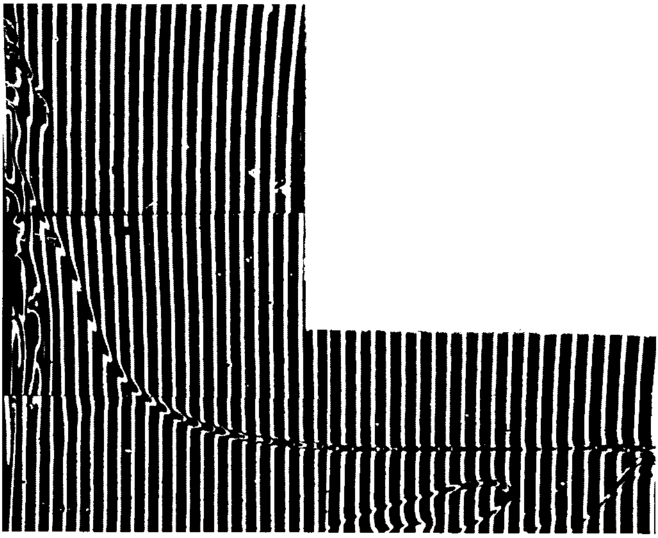


Figure 14
Several Interferograms of Wide Seal

nature of the layers left on glass after heaing by flame. The effect of temperature on the alkalies release was studied in the temperature range of 750°F. to 1100°F. (400°C. to 600°C.) by an instrument described in section 3.2 and shown in Fig. 4. The results are presented in the graph of Fig. 15. The curve 1 shows the amount of sodium collected on the target and curve 2 the amount extracted from the tested samples by water. These two curves are of opposite directions. In curve 1 only a negligible amount of alkali was collected at low temperatures. On the other hand, in curve 2, at the same low temperature region, high amounts of sodium are taken out into solution. Starting at about 980°F. (530°C.), the sodium was evolved in large amounts and almost linearly with temperature with a high slope of 8.2 micrograms per F°. On the other hand, the sodium extracted by solutions decreased to a very low value (14 mg. at 1100°F.) for the same high temperatures. The unheated sample released 368 micrograms. The amount collected on the target together with the amount taken into solution at any paricular temperature never equalled to the above control of unheated sample (highest only 337 micrograms). This is very important, because it quantitatively supports the theoretical considerations described in part 2 and visually demonstrated by interferograms in part 4 of this paper. It was postulated that a siliceous layer is formed which because of its higher viscosity slows down further diffusion of alkalies to the surface from internal layers. The two independent techniques (namely interferometry and alkalies release) clarified the situation of flamed surfaces which can be now stated in a concise and precise form: "—Flamed glass surface loses alkalies and changes to harder glass which does not allow replenishing of alkalies by migration from internal layers.—"

4.4 *Fluorine Release from Glasses*

Fluorine release from glasses was studied with equipment as shown in Fig. 5. Liquid nitrogen can condense all fluorine gases and it was first used. Later we employed dry ice bath and found that also all fluorine was collected. Dry ice can condense fluorine only in the form of hydrogen fluoride and alkali fluorides and cannot condense silicon tetrafluoride. This investigation was carried out at annealing temperatures of the glasses 900°F. (480°C.). Lately we started some preliminary investigations at sealing temperatures and here is an indication that fluoride can leave as silicon fluoride at elevated temperatures of sealing. Interferogram in Fig. 14 shows that the fluorine is quite instrumental in combating the highly siliceous layer left at the sealing edge after alkalies are driven out. Further investigations are in progress, and it looks like our theoretical considerations of section 2 will be proven right.

5. CONCLUSIONS

1. This work was presented to show that great benefits can be derived in the art of glass sealing from examinations employing modern tools. Furthermore the basic knowledge of glass technology can be enriched and fundamentals of what is happening during flame contacting glass can be formulated to higher precision. Applications to the glass sealing problems of the fundamentals were discussed in considerable detail.

2. Alkalies are released during heating the glass by flame.

3. The glass surface is richer in silicon which slows down further alkalies diffusion from interior.

4. It was shown that theoretically ideal glass-glass seals can be made by an operation guided by interferometrical examinations and by proper interpretation of the involved fundamental principals.

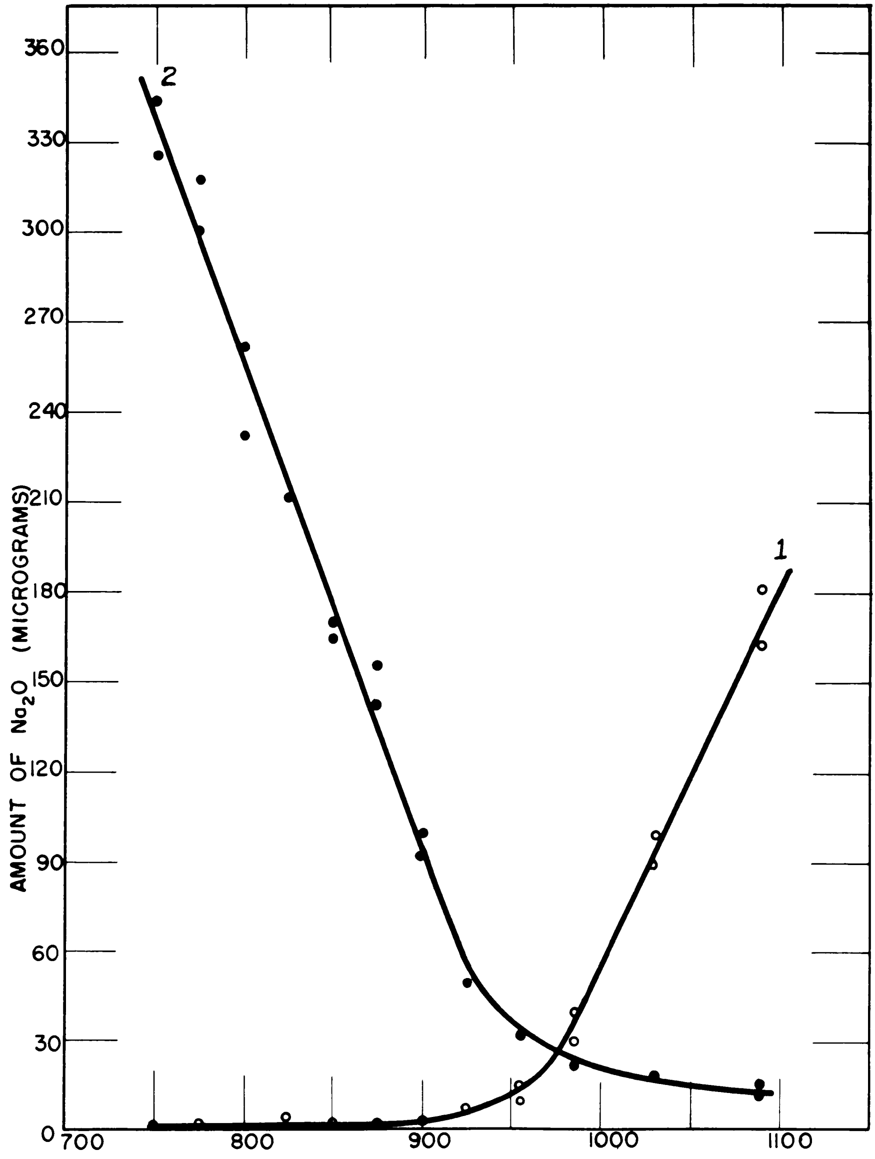


Figure 15

Evolution of Sodium and Release of Sodium into Solution

5. Small amounts of fluorine helps to equalize the decrease of alkalies during flame application. At annealing temperatures no silicon tetrafluoride is evolved.

6. Immersion interferometry is a tool which gives more information about glass sealing than any other technique employed before.

CERAMICS FOR ELECTRON DEVICES

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ABSTRACT

Application, property tests and preparation for various types of ceramics, and metal to ceramic seals used in electron devices will be discussed.

GLASS IN SPACE

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This era in which we now find ourselves is one filled with the fulfillment of some of Buck Rogers' and Jules Verne's wildest imagination. The rapidity with which technology is advancing is catching most of us by surprise. One of the problems with which we are faced is that of knowledge and how to acquire it. We do not have the luxury of a period of grace whereby all development ceases while mankind catches up. Instead, we find that by the time we can learn about and adjust to new concepts, it is obsolete. Let's go back, just 11 years, to 1950, and try to list the major areas of technological advancement. We find this a very difficult task indeed:

Jet Propulsion—Fast and Efficient Transportation
Transistors—Miniaturization and Low Power Requirement
Space Travel—Earth Orbit, Moon and Venus Probes
Astronomy—The Radio Telescope
Atomic Energy—Electrical Power

These are but a small percentage of the total that has been accomplished. Going back further, I feel that it had probably taken at least 25 years to make the equivalent gains as shown in these past 11 years. Probably before this, 50 years were needed to accomplish the same degree of specialization. We can no longer expect to be able to operate under the "Jack Of All Trades" concept. The different industries are growing farther apart. This is to be expected. The consultant is probably the best answer for those desiring and needing a liaison. However, this specialization is also occurring within industries and the results are more spectacular because the effect hits closer to home. Here, because of Government regulations, it becomes more difficult to maintain any level of contact except thru trade journals which usually present "after the fact" information. Finally—we have the specialization within companies. The larger the company, the greater the problem. Channels of communication are becoming as complex as the degree to which we specialize. Not only are we faced with difficulties of obtaining information but we find ourselves faced with a language barrier as well. Words by themselves, do not mean anything unless they have definition which is understood identically by the persons speaking and by those listening to them. You here are all specialists, or perhaps I should better say, specializing in similar areas of endeavor within companies—both in the same and different industries. I dare say that if you think about it, you will admit to difficulties at times trying to understand what is being told to you, both because the concepts are new or different, and the words used are strange.

This is the type of situation that exists between various air frame manufacturers and myself as we attempt to resolve the problems of design for the viewing areas on the different high performance manned flight vehicles. A little background history might help at this point—Ever since the aircraft industry began using glass extensively as windshield material, they have taken over more and more of the handling of design and specifications. This came about as a natural outgrowth of the knowledge they acquired over a period of years about the material—glass, as it related to their windshields. This knowledge was based on soda lime type glass under a relatively small number of conditions to which the glass was normally subjected. Up until recently, very little trouble was experienced with the glass. Primarily this was due to the tendency to overdesign in order to obtain a high safety factor for mechanical loads. As a result, little or no attempt was made to create specialists in glass, or at least to establish an effective liaison with the glass industry. To them, glass was glass. It was all the same—windshields, windows, bottles, light bulbs. To me, on the other hand, the term "glass" connotes about the same as the word metal does to people in the metal industry—very little. As you know, we in the glass industry can effect a parallel with the metals industry quite easily. We have families of materials too, soda lime, borosilicate, alumino silicate, etc. These to us mean much the same as steel, copper, silver, etc., do to the others. Even this breakdown is not enough to define a particular material. Alloys are created within each family, which result in the final characteristics or properties being sought.

The big problem was to be able to convince the aircraft industries—"glass experts" that they needed help. It wasn't that they weren't receptive or willing to be shown, it was just that communication barriers in the past had caused an improper interpretation.

We were able to show how the environmental conditions to which glass on aircraft, even today, is being subjected makes it an absolute necessity to perform the most rigorous of evaluation in order to obtain the proper glass, having the optimum processing and testing in order to achieve the degree of reliability required. Just as people are becoming more specialized—the need for the more specialized glasses is becoming greater.

In any manned flight vehicle the level of reliability is extremely high and as these vehicles become more exotic, it becomes a tremendous task to interpret what the effect on glass will be in order to design with the proper combination such that the reliability is not affected. This makes it extremely important that a complete exchange of information be accomplished between the vehicle manufacturer and ourselves as the glass designer. Neither one of us can perform effectively without all the facts to go on. Each is a specialist, and as I have pointed out before, the only way to marry the needs of one to the knowledge of the other is thru proper communications.

Let's look at what would happen to one of the simplest of these new high performance vehicles if current standard aircraft designs and materials were to be used.

Assume a windshield panel of a size 28″ long by 7″ wide having a thickness of 3/8″. The basic problem is concerned with heating caused by friction of air molecules as the vehicle forces its way thru them. This aerodynamic heating is transferred by conduction from the boundary layer to the surface of the glass windshield panel. This boundary layer is only a few thousandths of an inch thick, but the temperature gradient thru it is sufficient to reduce to a considerable degree the temperature that plays on the glass itself. Even so, temperatures in the order of 600°F. are reached at the surface.

Now, to compound the problem, add a mounting condition where the glass is held in a channel of Iconel or stainless steel and the edge is gasketed with asbestos. These are all the needed components to create a catastrophic effect.

First, assuming that the vehicle design is able to accomplish the ideal laminar or smooth flow of the boundary layer—which is not always the case—the protuberance of the mounting frame into the air stream causes turbulent flow at the leading and trailing edges of the panel. This, in turn, causes an additional temperature rise of up to 100°F. in very localized areas next to the frame.

Secondly, the rate at which this heating occurs is measured in seconds—not minutes.

Now, thru the 3/8" glass thickness, a thermal gradient of approximately 500°F. is established from the outer to the inner surface. This is the point where we have found that the design will trap those who do not understand what to expect from the properties of glass. The panel—initially called out to be made of soda lime type glass because this *is* glass to most persons—may take the shock of the temperature rise if it is fully tempered. But, now, let's see what else happens. The panel wants to deflect outward because of the temperature gradient. In fact, under these conditions, this deflection will be about 3/4" at the center. Now, if the panel were free to deflect, there would be no induced stress. But the mounting frame, which also is being heated, tends to elongate in a transverse direction, and effectively restrains the glass panel. We also have the condition whereby the asbestos gasket between the glass edge and metal channel frame is a good insulator. So with cold edge, combined with a hot center, we have a large thermally induced tension component acting along the edge and, as you know, glass fails only from tension components. Also, because of the steep gradient thru the glass—except at the edge, where deflection is imposed yet is restrained by both the retainer and the cold edge—we have a large, mechanically induced tension component. The result is a composite tensile stress in the edge area that approximates 20,000 psi. To this is added the stress produced by pressure differential exterted upon the panel from the flight profile and the cockpit pressures. The overall result is a very unreliable product which undoubtedly would fail.

It might be of interest to mention some of the basic processing criteria and testing procedures which we have determined to be of prime importance in order to insure the highest possible level of product reliability. These are concerned only with the glass itself. Effect of the design on shape, thickness, mounting technique, etc. are secondary to this preparation. In other words, even a perfect design is of no value if the glass itself is not reliable.

1. The surface preparation, *i.e.,* grinding and polishing, is to be done cold and easy. This is to minimize the condition whereby checks become driven into the body of the glass, yet are undetectable because they close up from residual stresses and then become smeared over in polishing.

2. Edges should be rounded with a radius equal to 1/2 the thickness of the panel. This is to reduce the incidence of handling damage as well as to smooth out stress patterns.

3. Edge grinding should be done with not less than 220 grit and the direction of grind should be parallel to the surfaces.

4. Each panel shall be subjected to thermal shock. The up-shock is to eliminate internal flaws caused by knots and stones. Down-shock is to subject the surface to a tension force of about 7500 psi fibre stress. This test is to act as process control over all of the manufacturing processes performed on the glass up to the point where the test is made.

5. The edges should be acid polished. This is to round off the sharp angles on the "hills and valleys" caused by grinding.

We feel that by having the above conditions included in all specifications for glass on high performance vehicles, the reliability factor would be improved by a factor of at least two.

Looking forward now to some of the plans being made for the more exotic and refined space travel we find ourselves being confronted with environmental conditions never before encountered. In fact, there is very little if any practical data available to support any of the design criteria. To illustrate—consider the following list of environmental conditions and requirements in terms of their combined effect on a window package design:

1. Good optics from normal viewing angles to up to 60° off normal, with the retention of fair optics even after exposure to 2200°F. to facilitate landings.
2. Launch shock of up to 40 g. at a rate of 8000 g./sec.—with static acceleration of 18-20 g.
3. Launch vibration of 20-1200 cps at 150 db.
4. Orbital or space flight profile in hard vacuum including a wide temperature variation when facing towards or away from the sun.
5. A seal between the enclosure and window components such that *no* air leakage is permitted.
6. Micrometeorite impact at velocities up to 80,000 ft./sec.
7. Radiation shielding without discoloration.
8. U. V. shielding such that a cut-off at 3800 angstroms could be made.
9. Re-entry temperatures up to 2400°F.
10. Shield occupants from effect of 2400°F.

Windows that might be used for camera or navigational functions require a much higher degree of optical clarity, yet still must meet most of the aforementioned environmental conditions.

Let's examine these conditions more closely to see what has to be considered in order to select glass type and determine processing characteristics.

1. Good optics for viewing angles up to 60° off normal.

First off, the window or viewing unit will have to be made of more than one panel—probably 4 or 5 would be realistic. Angular vision through 4 or 5 panels is not going to be good. The loss in transmission caused by long glass paths—and the reflections from all those surfaces—will reduce visibility to practically nothing. A significant gain can be made, however, by an application of a coating of Mgf on many of the surfaces. This coating, when applied in properly graded thickness, can reduce reflections to a point where they are not detected. Normally, if a window package of this type ends up with a total transmission in the order of 40%, satisfactory viewing can be achieved.

2. Launch Shock

This conditions can be accommodated thru a rigid mounting frame and good gasketing on the edges of the glass. Of course, results will depend on the position of the glass in relation to the direction of shock. Normally, the glass would be in an "edge-on" direction, which would result in only a compression moment—plus edge impact. However, if by some weird requirement the glass was normal to the shock, it would mean a tremendous increase in panel thickness as well as mounting frame "beef up".

3. Vibration

Cushioning or damping between glass and frame and/or frame and vehicle body will be required. Also, a test would be necessary to determine whether the particular type of glass and its shape and thickness would set up harmonic vibration.

4. Exposure to extreme vacuum under various levels of changing temperature.

Except for the pressure differential that would be induced, it is not expected that vacuum would be detrimental. The effect of temperature variation would be reflected only in different expansion or contraction characteristics between the glass and the metal framing member.

5. Positive seal of the glass to vehicle.

This is probably the most important condition that would have to be met, especially if the mission is to be in space for a significant length of time. The problem is that the vehicle will have to carry its own regenerating oxygen supply. Any leaks will reflect in loss to this supply, and due to weight and storage limitations, there would not be much leeway allowed for excess supply. It, therefore, will be necessary to make a glass-to-metal seal—capable of withstanding the shock and vibration loads, as well as temperature and pressure differentials—as well as being capable of patching in flight, if a leak does develop.

This leads to a suggestion for a glass inner capsule liner due to the non-porosity of glass. If this ever were considered—and this is not as far-fetched as it might seem—you people, as lampworkers, would certainly be faced with a tremendous challenge.

6. Micrometeorite impact.

There is no data as to what the effect on glass might be. The particles are extremely small, .005″ to .0005″ in diameter. Depending upon time in space, it could be expected that several thousand impacts might occur. What data there is, has been extrapolated from Discoverer and Explorer satellites which carried equipment that recorded number and energy of impacts. The best guess to date is that only a pitting would result. The probability of impact by particles significantly larger than indicated is based on statistical means. If such impact does occur, obviously a catastrophic failure would result.

7. Radiation shielding.

This presents no problem except as related to the total time of exposure and to the type of radiation. Normally, fused silica glass will handle the condition without discoloration.

8. Ultra-violet radiation.

This is the portion of the spectrum which causes burning of the skin as well as damage to the eyes. In order to perform an absorption function, a filter glass would have to be selected that would have sharp cut-off characteristics at around 3800 angstroms. Probably a new glass would have to be used to more closely meet the given mechanical and thermal conditions plus having the ultra violet cut-off.

9. Re-entry temperatures up to 2200°F.

The deciding factor here is the amount of time at this temperature under the concomitant factor of pressure. Fused silica could meet this requirement if the other criteria were right. It may be necessary, however, to have a sliding metal shield that would cover the window area during this portion of the flight.

10. Protect occupants from the infra-red radiation at the 2200°F. re-entry temperatures.

This again involves functions of temperature and time. For relatively short times—say 5-10 minutes—the use of multi-panels, with an infra-red reflectant coating on the surfaces should do fairly well. Air gaps between panels will inhibit transfer by conduction and convection. The IR coatings will reflect a high percentage of the energy at these wave lengths.

For longer periods of time, the sliding metal shield appears to be the best solution.

I have not discussed the extreme range of problems being faced by those concerned with high performance manned flight. In both current vehicles and future space flight programs, there are many conditions that are new and different. Much more thought has to go into the design of glass than ever before. It rests with the glass industry to see that glass remains in use even in the face of difficulties that merely *appear* to be insurmountable. This can be accomplished thru a ready willingness to learn about the problems of others, teach the learning of our profession, and be free with creative imagination.

HIGH TEMPERATURE GLASSES

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1. INTRODUCTION

Glassmaking is limited to compositions chiefly by ease of fusibility. With the attainment of high temperatures and better refractory materials for containers it has become possible to commercially produce higher annealing point glasses heretofore considered impractical to melt on a large scale. Until the advent of reconstructed glasses, fused silica was considered the ideal material for most of the uses to which glass is put. Difficulties are encountered in producing clear, bubble-free ware of fused quartz because of its extremely high viscosity exhibited at its melting point and the extremely high temperatures necessary for working this glass. These difficulties have been overcome by the Hood-Nordberg process[1], a unique process for making high silica glasses from a base glass of apparently normal characteristics. A description of this process was given by M. E. Nordberg in earlier publications[2,3] but is again briefly discussed here under the heading "Reconstructed Glasses". It is the purpose of this paper to describe some of the properties and applications of these high silica glasses which are commercially sold under the trademark "VYCOR". To complete the discussion, comparisons are also made with other high melting glasses such as Corning's Code 1715, 1720, and 1723 calcium alumino-silicate glasses.

2. GLASSES PREPARED BY DIRECT MELTING

The viscosity characteristics of glasses are important to both the chemical and electrical industry. The need for glasses possessing high resistance to deformation at elevated temperatures is increasing with advancing technology. This has led to renewed interest in the production of high temperature glasses. Fig. 1 shows viscosity-temperature curves for a number of technical glasses. In order to free glasses from bubbles it is generally necessary to melt at temperatures where the glass viscosity is about 10^2 poises or lower. Moderate temperatures are needed for melting high lead (Code 8870), potash soda lead (Code 0010) and soda lime (Code 0080) glasses. These glasses have relatively low annealing points. (Note temperature corresponding to viscosity 10^{13} poises—value 13, on the vertical axis in Fig. 1). Aluminosilicate glass, Code 1710, is rather interesting in that despite the fact that it is an appreciably more fluid glass at 1500°C. than low expansion borosilicate Code 7740 glass, it sets up more rapidly and possesses higher viscosity at lower temperatures than Code 7740.*

E. B. Shand[4] has tabulated temperatures which must be attained at the surface of various glasses during tank melting. These are reproduced in Table I.

TABLE I

GLASS MELTING TEMPERATURES

Glass	*Melting Temperature Surface of Glass, °C.*
Soda-lime	1500
Lead silicate	1450
Borosilicate, low expansion	1600
Aluminosilicate	1600

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*Viscosity curves of these glasses are also shown in Fig. 1.

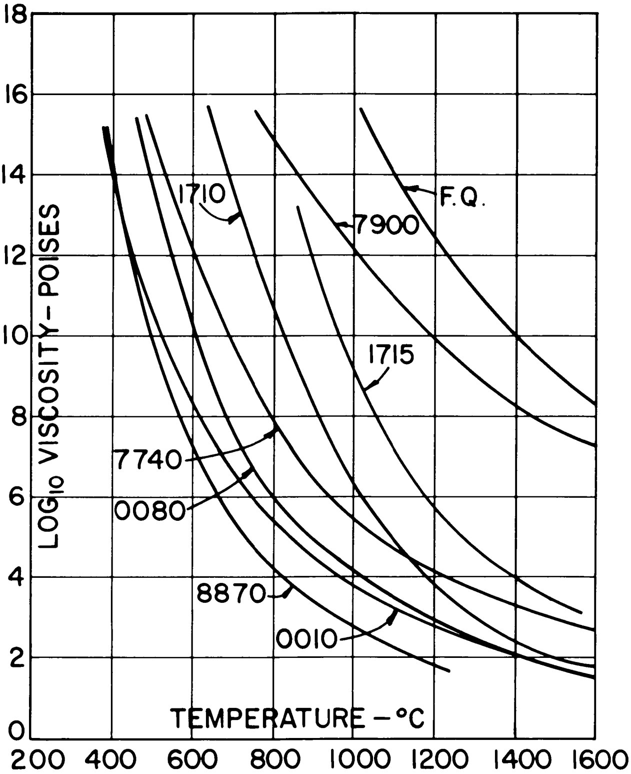

Figure I
Viscosity curves of various commercial glasses. Code 8870: high lead; Code 0010: potash soda lead; Code 0080: soda lime; Code 7740: low expansion borosilicate; Code 1710: aluminosilicate; Code 1715: hard tungsten sealing aluminosilicate; Code 7900: 96% silica; F.Q.: fused quartz.

In order to successfully melt aluminosilicate glass, Code 1715, it is necessary to use temperatures near 1800°C. Temperatures of this order of magnitude are readily obtained in melting units by using oxygen instead of air for burning the gaseous fuel. This glass has an extremely steep viscosity curve. See Fig. 1.

The viscosity curves for VYCOR Brand Code 7900 glass and fused quartz are also shown in Fig. 1. Glasses having their compositions cannot be prepared by conventional melting methods. Pure Brazillian quartz is generally used as raw material for making high quality silica glass. Code 7900, a glass which approximates fused quartz (silica glass) in many of its properties, is one of the "lesser hard" glasses in a family of glasses which can be made by the Hood-Nordberg process[1].

3. RECONSTRUCTED GLASSES

Reconstructed glasses, more generally known under the trademark, "VYCOR", are made by a process invented by H. P. Hood and M. E. Nordberg[1] whereby a special soft alkali-borosilicate glass is melted and formed to the desired but oversize shape in the conventional manner. After a heat treatment at temperatures above the annealing point but below that which would give serious deformation, the glass can be safely leached in a hot dilute solution of a mineral acid. Practically all constituents except the silica are removed during leaching. At this stage the glass is porous, containing millions of interconnecting pores. The composition of the porous glass on the basis of its ignited weight is 96% SiO_2, 3% B_2O_3, 0.4% $R_2O_3 + RO_2$ (chiefly Al_2O_3) and traces of Na_2O and As_2O_3. The porous glass is known as VYCOR Brand glass Code 7930, but has also been referred to as "thirsty glass" because of its affinity for moisture. Some of its properties have been described by M. E. Nordberg in previous publications[2,3]. After the acid treatment the porous glass is dried to remove capillary water and fired at high temperature to consolidate the porous structure and shrink the glass article to its finished size.

A whole family of VYCOR Brand glasses can be made by varying the conditions of heat treatment, leaching, prefiring, and firing, or by subjecting the glass to additional processing steps, such as for example, impregnation with various coloring oxides prior to consolidation. The family of low expansion VYCOR Brand glasses have annealing points near the upper end of the curve shown in Fig. 2.

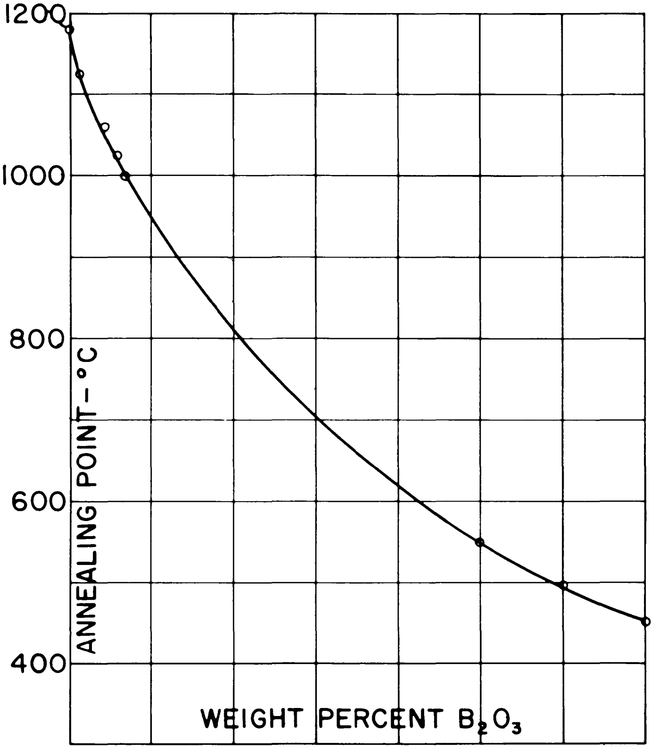

Figure 2

Effect of B_2O_3 on Annealing Point of Binary SiO_2-B_2O_3 Glasses. Viscosity at annealing point is 10^{13} poises.

4. PROPERTIES OF SOME RECONSTRUCTED GLASSES AND OTHER GLASSES

4.1 *Ultraviolet Transmittance*

Glasses transparent to ultraviolet radiation are used in ozone lamps, germicidal lamps, sun lamps, blue-print lamps, high pressure lamps for outdoor lighting, high bay lighting, and other purpose lamps. Glasses for these applications must be chemically compatible to mercury vapor at elevated temperatures and to humid atmospheres in which the lamps might be used. They must also not solarize in use.

Because small variations in minor constituents have an appreciable effect on the ultraviolet transmittance it is imperative that the batch materials, refractory materials for containing the glass, and melting conditions are closely controlled. These requirements and other factors make production of glasses with high transmittance at far ultraviolet wavelengths (1850-2800 Å) by conventional melting methods very difficult, if not impossible. Most direct melted glasses are subject to solarization, that is they show a marked loss of transmittance from exposure to ultraviolet radiation. This decrease is greatest in the far ultraviolet wavelengths and is generally less pronounced in the middle and near ultraviolet wavelengths, 2800-3200 Å and 3200-3800 Å respectively. The Hood-Nordberg process for making reconstructed glasses is ideally suited for making ultraviolet transmitting glasses since it is possible to exert considerable control over the ultraviolet transmittance by varying leaching and firing conditions.

The ultraviolet transmittance of Code 7900, 7910 and 7912 glasses are compared in Fig. 3 with that of PYREX Brand glass, Code 7740. Code 7900 glass shows an appreciable drop at shorter wavelengths which is attributed to traces of ferric oxide. This glass is intended for general use and is therefore not controlled for ultraviolet transmittance. Code 7910 and 7915 glasses both transmit well in the ultraviolet. A typical curve for the latter glass is given in Fig. 4.

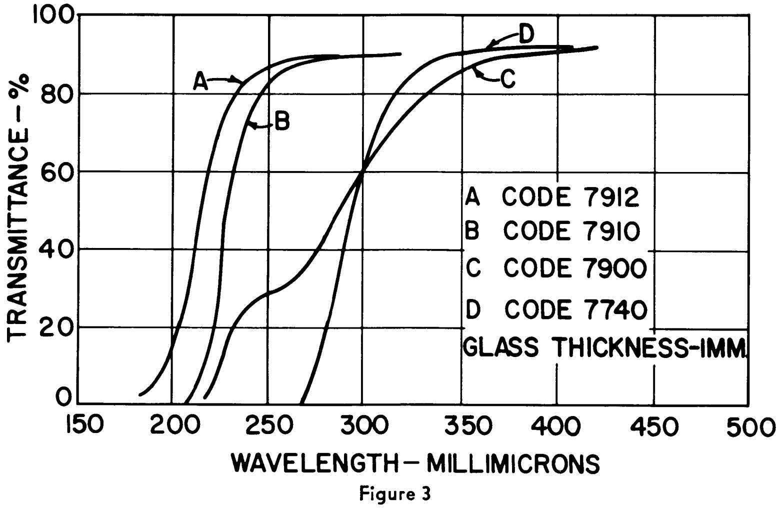

Figure 3

Ultraviolet transmittance of some VYCOR Brand high silica glasses (see Section 7) and low expansion borosilicate glass Code 7740.

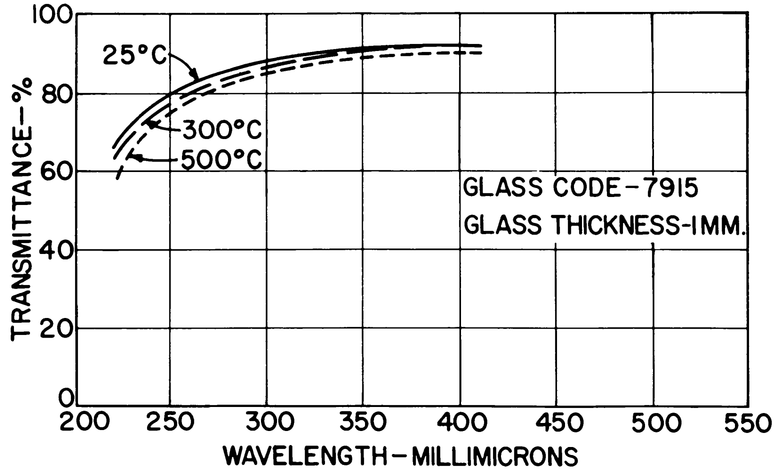

Figure 4
Effect of temperature on ultraviolet transmittance of VYCOR Brand Code 7915 glass.

The effect of temperature on ultraviolet and visible transmittance has been recently studied by W. A. Plummer[5] for various glasses including VYCOR Brand glasses Codes 7900, 7905, 7910 and 7915. His results for Code 7915 glass are shown in Fig. 4. According to Plummer, the general effect of temperature is to produce a shift in the short wavelength cutoff towards the longer wavelengths. The magnitude of this shift varies with the type of glass, but happens to be relatively small in the case of VYCOR Brand glasses.

The ultraviolet transmittance of reconstructed glasses is not limited to the examples shown in Figs. 3 and 4 but can be engineered to produce additional glasses with cutoffs at nearly any desired wavelength in the ultraviolet spectrum.

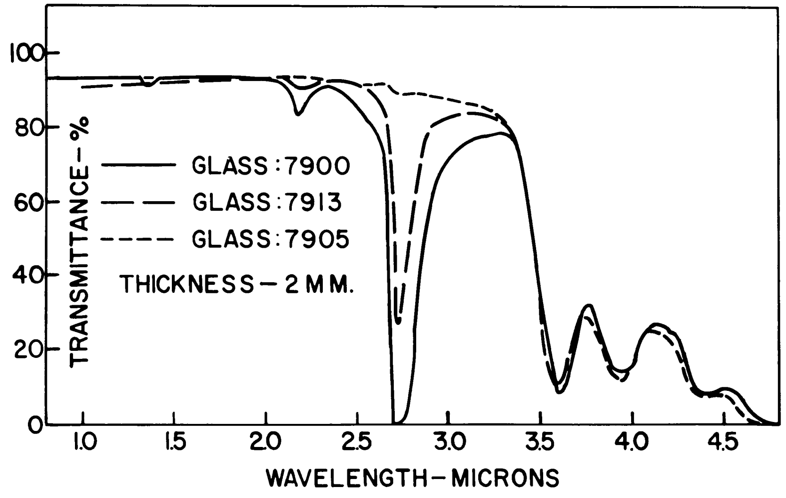

Figure 5
Infrared transmittance curves for several VYCOR Brand high silica glasses.

4.2 *Infrared Transmittance*

The infrared transmittance of Code 7900, 7913 and 7905 glasses at 2 mm are given in Fig. 5. The first two glasses have a relatively sharp absorption band at 2.72 micron wavelength which is attributed to traces of water in these glasses. Code 7905 glass does not show this band because it is a water-free glass. It shows practically no decrease in transmittance at wavelengths up to 3.3 microns.

Infrared studies at temperatures of 25, 300 and 600°C. by C. J. Parker and M. E. Nordberg, Jr.[6] have been made on various glasses. They found that for VYCOR Brand glasses the changes in transmittance are relatively small in this temperature range.

4.3 *Outgassing*

It has been shown by various investigators[7] that when glass is heated at temperatures below the softening point, gas, consisting primarily of water, is evolved from the glass.

To assure long service life, glasses used in lamp and electron tubes operating at elevated temperature must not evolve appreciable volume of gases during operation. In the case of reconstructed glass, the outgassing characteristics can be engineered by degassing the glass prior to and during consolidating the pores. This is illustrated in Fig. 6 which compares the outgassing behavior of Code 7900

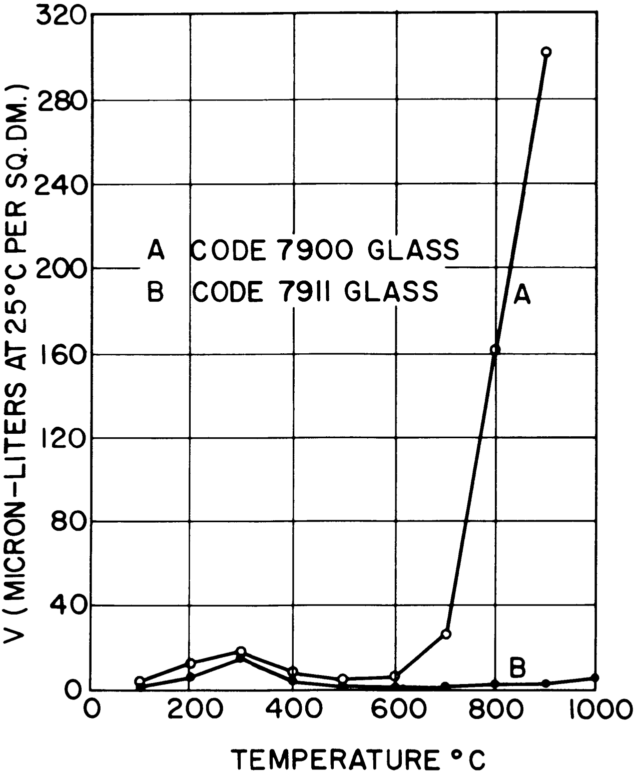

Figure 6
Outgassing curves for two VYCOR Brand high silica glasses. See Section 4.3.

glass against Code 7911 glass[8]. The latter glass is especially degassed in manufacture. The volumes expressed in microliters at 25°C. per square decimeter of sample surface in Fig. 6 are the volumes evolved during 2½ hours bake-out at temperatures shown on the horizontal axis and do not include the volume evolved in any previous bake-out. Prior to baking at 100°C., the glasses were evacuated for one hour at room temperature.

Another form of outgassing takes place when glasses are subjected to ultraviolet light and subsequently or simultaneously baked at elevated temperatures. The effect of such radiation on outgassing characteristics of glass is presently being studied to learn more about what happens during burning of mercury vapor lamps. Preliminary work indicates that unlike conventionally melted glasses, VYCOR Brand glasses do not show any appreciable outgassing under these conditions.

4.4 *Helium Diffusion*

The diffusion of helium through various glasses has recently been investigated by V. O. Altemose[9]. He confirms the finding by F. J. Norton[10] that the relative permeation is a function of the proportion of glass-forming oxides in the composition. Table II gives relative diffusion rates for helium in some of the glasses measured by Altemose. The diffusion rate of Code 1723 glass, an aluminosilicate glass, at 200°C. was arbitrarily chosen as 1. Its actual permeation constant at 200°C. (extrapolated value) is 2×10^{-13} cubic centimeters of helium (at standard temperature and pressure) per second per square centimeter surface per millimeter thickness per centimeter of mercury pressure difference. Altemose also showed that at this temperature hydrogen permeates through Code 7900 glass at about a fifty times slower rate than helium. VYCOR Brand glasses and fused quartz are much more pervious to helium and hydrogen and for all glasses, permeation increases markedly with temperature. The rate of this increase is greatest with the least permeable glass.

TABLE II

HELIUM DIFFUSION

	Relative Diffusion Rates		
Glass	200°C.	400°C.	600°C.
Code 7900	5.8×10^3	2.6×10^4	6.0×10^4
Fused Quartz	4.6×10^3	2.0×10^4	4.6×10^4
Code 7740	1.1×10^3	8.0×10^3	2.5×10^4
Code 1715	2.8	1.4×10^2	1.2×10^3
Code 1723	1	26	2.6×10^2

4.5 *Electrical Properties*

Reconstructed glasses are finding increased usage in electrical industry, especially in the lighting field, because they not only possess excellent electrical properties but also are able to operate at high temperatures, transmit visible light, infrared and ultraviolet radiation. The electrical resistivity is higher and dielectric loss is much lower for these glasses than for ceramics and glasses in general. Table III shows that Code 7913 and 1950 glasses both have high resistivity and low power factors. The latter has electrical characteristics comparable to the highest quality fused quartz.

TABLE III

PROPERTIES OF HIGH TEMPERATURE GLASSES

	Fused Quartz	*Code 1950*	*Code 7913*
Exp. Coef. per °C., (x 10^{-7})	5.5	6.8	7.5
Annealing Point, °C.	1140-1190	$>$1060	$>$1020
Electrical Properties			
Log_{10} R at 350°C., ohms-cm	9.5	9.7	$>$8
Power Factor at R.T. and 1 M.C., %	$<$0.02	$<$0.01	0.04
β(OH), mm^{-1}	0.01	$<$0.0165	$<$0.4

β(OH), the absorption coefficient for water at 2.72 micron wavelength is calculated by means of the following equation:

$$\beta(\text{OH}) = \frac{1}{t} \log_{10} \frac{T_1}{T_2}$$

where t = thickness of glass in mm

T_1 = transmittance at 2.6 μ wavelength

T_2 = transmittance at 2.72 μ wavelength

Properties are given in Table IV for a number of aluminosilicate glasses which offer many advantages in the design and construction of rectifiers, power, cathode ray and microwave tubes. The volume resistivities at high temperatures of Code 1723 and 1715 glasses are among the highest in any commercial glass. See Fig. 7. Their higher annealing points permit higher bake-out temperatures and higher operating temperatures than hitherto possible with conventionally melted glasses.

The properties of Code 1950 glass, also listed in Table IV, will be discussed under high pressure mercury vapor lamps under Section 5.

TABLE IV

PROPERTIES OF SOME ELECTRICAL GLASSES

	Code 1720	*Code 1723*	*Code 1715*	*Code 1950*
Exp. Coef. per °C., (x 10^{-7})	42	46	35	6.8
Annealing Point, °C.	715	712	866	$>$1060
Electrical Properties				
Log_{10} R at 250°C., ohms-cm	10.8	14.1	13.8	11.4
Log_{10} R at 350°C., ohms-cm	9.0	11.7	11.5	9.7
Power Factor at R.T. and 1 M.C., %	0.37	0.14	0.26	$<$0.01

The Na_2O content in Code 1950 glass is maintained below 20 p.p.m.

4.6 *Devitrification*

Cristobalite, one of the crystalline forms of silica, is formed when reconstructed glass or fused quartz undergo devitrification at elevated temperatures. The rate of devitrification is very low for these glasses provided they are clean and heated in a contamination-free atmosphere. It becomes appreciable, however, when mineralizers are originally present on the glass surface or in the atmosphere.

The devitrification of VYCOR Brand Code 7913 glass and fuzed quartz has been studied at 800 and 850°C. with small plates placed over porcelain crucibles

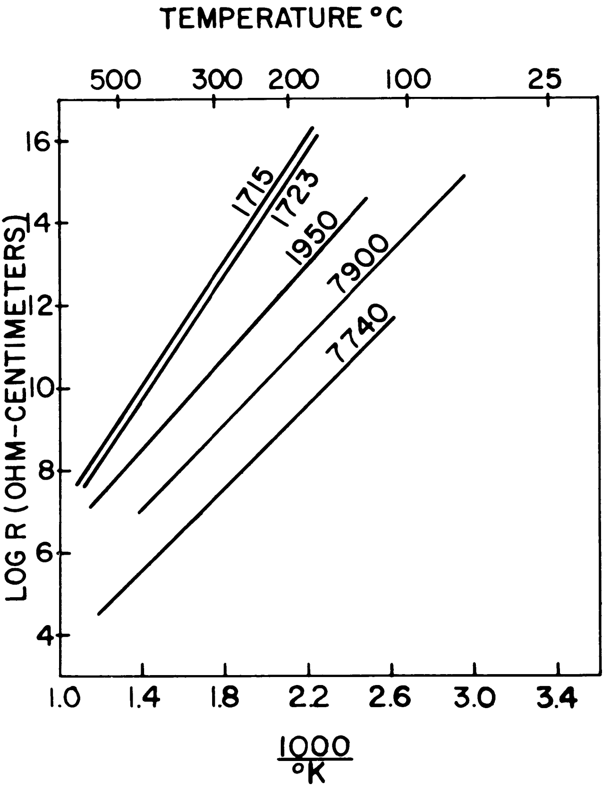

Figure 7

Volume resistivity, in terms of $\log_{10}$ R, as a function of temperature for various glasses. Code 1715: hard tungsten sealing aluminosilicate; Code 1723: aluminosilicate; Code 1950: nearly 98% silica with less than 0.002% Na_2O; Code 7900: 96% silica; Code 7740: low expansion borosilicate.

containing sodium carbonate. By observing the frosted spot in the glass plates resulting from inversion of β-cristobalite to α-cristobalite as the devitrified samples are cooled to below 300°C. one can get some idea as to the degree of devitrification which has taken place on the faces of the plates exposed to sodium carbonate vapors. For fire-polished Code 7913 glass the diameter of the spot was roughly one-half that observed without fire-polish. No significant difference in devitrification was found however between fire-polished reconstructed glass and fire-polished fused quartz plates at the temperatures used in these tests. The duration of the tests ranged from 1 to 10 days at 800°C. and 1 day at 850°C. No devitrification was observed at these temperatures when sodium carbonate was absent.

Alkalies, such as for example sodium carbonate used in above tests, are mineralizers which greatly accelerate devitrification at elevated temperatures. Mere traces of alkalies, such as would be left by finger prints, on the glass surface have a pronounced effect and should, if possible, be avoided. To insure absence of such contamination, the glasses should be washed in acid or treated in hydrofluoric acid and thoroughly rinsed in distilled or demineralized water. The cleaned glasses should then be handled with clean gloves or clean tools.

In both VYCOR Brand glasses and fused quartz, devitrification starts at the surface and progresses slowly into the body of the glass. A heavily devitrified surface crazes on cooling due to the large volume change which accompanies the cristobalite inversion at below 275°C. Crazing can be prevented by not allowing the glass to cool below about 300°C. This is possible in some applications and prolongs life at higher temperatures. If occlusions are present, such as bubbles or elongated seeds found in most of the commercial fused quartz, devitrification may also be observed in the interior of the glass where these defects are located and may lead to internal cracking of the article.

At elevated temperatures devitrification can also be promoted by electrical fields. This effect can be readily observed by subjecting strips of glass to a direct current voltage gradient at 900°C. for a period of one or more days. In our tests the electrodes are 1½″ apart and the voltage was 540 Volts D.C. A small white spot develops at the negative electrode. It is caused by migration of alkali ions under the influence of the electric field. The size of the spot has been found to vary directly with alkali content in the glass. As the alkali continues to concentrate, it causes the glass to eventually devitrify accounting for the appearance of the spot. Devitrification of this type can be observed in high pressure mercury vapor lamps. In order to minimize the electrolysis effect, Code 7915 and 1950 glasses with extremely low alkali content were developed. These glasses are further discussed under high pressure mercury arc lamps.

4.7 *Lampworking Properties*

In earlier publications[2,3], M. E. Nordberg has pointed out that the lampworking properties of reconstructed glass are similar to those of fused quartz except that its working temperature is not as high. For this reason lampworkers find it generally easier to work than fused quartz. For all but large items, an oxy-gas flame is usually satisfactory. The white bloom produced on cooler areas adjacent to the heated area can generally be removed by heating, etching with dilute hydrofluoric acid, or buffing. The bloom consists of silica volatilized from the glass during lampworking. It can be minimized by preheating the area adjacent to that being lampworked.

Code 7900 glass in some forms may have a tendency to bubble on lampworking. This effect has been practically eliminated for the past two years in tubing and articles made from tubing. Code 7911 and 7913 glasses do not show this tendency because they contain appreciably less water than Code 7900.

One of the many advantages of reconstructed glasses is that by virtue of their very low expansion coefficient these glasses, unless in the form of large ware, can be heated quickly or even spot worked without fear of breaking and, furthermore, require much less annealing than higher expansion commercial glasses. If annealing is desired the ware should be heated to at least 950°C. for a few minutes and cooled. Slow cooling is unnecessary. Welding techniques, such as are used in flame-welding of metals, have been successfully used for sealing flanges to large tubing, or joining other large parts of glass.

The intentional addition of coloring oxides has been found to greatly alter the lampworking characteristics of reconstructed glass. In the case of radiant heat tubes made of red-stained VYCOR Brand glass Code 7950 more intense heating is necessary to flow the glass than for clear glass. These tubes are generally provided with integral clear ends to facilitate lampworking. Vanadium-containing reconstructed glasses have been made which are almost impossible to distort in a gas-oxygen flame although these glasses do not have a higher sag resistance than clear glasses when tested in a furnace. The tremendous increase in apparent "hardness" of the colored glasses observed in lampworking is brought about by the increased radiant emissivity and decreased high temperature conductivity resulting from the addition of the coloring oxide.

Since the aluminosilicate glasses have been mentioned in this paper it is but fitting that their lampworking characteristics be also discussed. Among Code 1715, 1720 and 1723 glasses, the former glass has the least tendency to reboil during flame working. The reboil tendency can be minimized or eliminated by careful attention to flame adjustments and the elimination of any contamination from dirt or fingermarks in the seal area. Gas-oxygen firing should be used. Oxygen settings are made less critical by the use of ethyl-orthosilicate as a flame additive.

4.8 *Maximum Operating Temperature of Reconstructed Glasses*

It is difficult to designate a maximum operating temperature for reconstructed glasses because of the many different ways and shapes in which these glasses may be used. For prolonged service in absence of corroding or devitrifying agents Code 7900 glass can be used up to 900°C. and Code 7913 at even higher temperatures. Heavy-rimmed shallow dishes such as calcining trays made of Code 7913 glass can be repeatedly used up to 1200°C. in short time applications. Tubing supported within refractory tube muffle furnaces have been successfully used for numerous short time firings up to 1350°C. Crucibles properly backed up with refractory to prevent deformation are advantageously used for melting high purity glasses at temperatures up to 1500°C. For vacuum work operating temperatures of the glass depends on thickness and tube diameter. For 1½ inch diameter standard wall tubing temperatures up to 900°C. have been used depending on glass type and duration of heating.

The rate of surface devitrification encountered at high temperature has been found to vary with furnace contamination. The devitrified layer on the surface is not necessarily harmful since it has a definite stiffening effect at elevated temperatures. However, if the tube is cooled to permit cristobalite inversion, as discussed earlier, it becomes more fragile. This effect increases with the amount of devitrification that has taken place at the high temperature and can lead to premature failure if the ware is not handled with care. In some applications, again as mentioned earlier, it is possible to increase service life at these high temperatures by not allowing the ware to cool below 300°C.

5. GLASS FOR HIGH PRESSURE MERCURY VAPOR LAMPS

High pressure mercury lamps, such as for example are used for highway lighting, must withstand severe service of long duration (up to many thousands of hours). The glass is exposed to strong ultraviolet radiations emitted by the excited mercury vapor and must be capable of resisting solarization effects to avoid a loss in ultraviolet and visible transmittance. The glass, furthermore must be sufficiently viscous at operating temperature to prevent deformation during the life of the lamp. Its alkali and water content must be carefully controlled to minimize electrolytic devitrification and outgassing, respectively, in service. Corning has developed Code 7915 and 1950 glasses which meet these requirements.

These glasses are nearly 98% silica. They both contain less than 0.002% Na_2O and the water content is, respectively, less than 0.003% and about 0.002% (determined by infrared absorption data). Aside from water content the properties of these glasses are nearly identical. They are listed under Code 1950 glass in Table III. Ultraviolet transmittance is shown for Code 1915 glass in Fig. 4. Infrared transmittance is comparable to that of Code 7905 glass shown in Fig. 5. Note the near absence of the water absorption band near 2.7 microns wavelength.

6. GRADED SEALS

Graded seals are used for joining reconstructed glasses to higher expansion glasses or metals. In the past, most seals were made by joining together a series of intermediate glasses by conventional lampworking technique or by the Multiform process. The latter process consists essentially of pulverizing the intermediate glasses, forming a composite tube of powdered rings differing successively in their expansion characteristic by methods simulating ceramic techniques, and refiring. By starting with porous glass tubes it is possible to make a one-piece graded seal from 96% silica glass. Alkali borates are introduced in the porous glasses by impregnation in such a manner that the expansion coefficient changes continuously in the final fired seal. Graded seals of this type are generally used for sealing fused quartz or 96% silica glass to low-expansion borosilicate glasses. They are available in sizes ranging up to 115 mm in diameter. By attaching additional intermediate glasses they can, of course, be sealed to even higher expansion glasses.

Under special conditions where metal rods, such as tungsten leads in xenon lamps, are subjected to high temperatures, harder intermediate sealing glasses than are normally used for tungsten sealing should be used to avoid deformation in manufacture or in service. Code 1715 glass which has an annealing point of 866°C. might be useful here. Code 1723 or 1720 with annealing points of 712 and 715°C., respectively, are recommended for molybdenum sealing.

There is no metal alloy that matches the low expansion characteristics of reconstructed glasses up to the setting temperature of the glass. Graded seals must be used for sealing to heavy metal leads. However, thin metal foil can be sealed directly in reconstructed glasses since it yields sufficiently to avoid breakage of the glass. In mercury vapor lamps, electrodes made of molybdenum foil 0.005 inches thick are successfully sealed directly into these glasses.

7. FEATURES AND APPLICATIONS OF RECONSTRUCTED GLASSES

Since 1940 when reconstructed glasses of very low expansion were first sold on the market under the trademark "VYCOR" there have appeared many new types of VYCOR Brand glasses. These are sold under various code numbers, some of which have been discussed above. It is not possible in this discussion to cover all the properties and special features of these glasses. Additional properties such as chemical durability, heat shock resistance, mechanical strength, abrasion hardness, and physical properties of porous glass have been covered in earlier publications by M. E. Nordberg[2,3,11] and in brochures on VYCOR Brand glasses.

Reconstructed glasses are generally made in the form of tubing, sheet, blown and pressed ware. Powdered Code 7900 glass is also slip cast or dry pressed and fired to consolidate the granules into an integral piece. This manufacturing process, also used with various powdered "soft" glasses, is known as Multiform process. It enables one to make massive ware or shapes that cannot readily be made by ordinary glass working techniques. Its applications will not be discussed here.

Some of the special features and applications of various VYCOR Brand glasses are given below. For convenience sake, the glasses are described in numerically increasing order.

CODE 7900—This glass has no restrictions on ultraviolet transmittance. Its water content is not controlled and in some forms it may consequently develop some seeds on lampworking. It is used chiefly in chemical ware and tubing for general laboratory use but is also available in sheet, and other blown or pressed ware.

CODE 7905—This glass is controlled for high infrared transmission below about 3 microns wavelength. An 0.125 inch thickness of Code 7905 glass will transmit a minimum of 80% at 2.72 microns. A typical transmittance curve of this glass is shown in Fig. 5. It is available in sheets, pressed ware and other forms. Code 7905 glass domes are used in heat sensing missiles which "see" or "home on" infrared waves.

CODE 7910—It is an ultraviolet transmitting glass specially prepared to transmit at least 70% at 254 millimicrons for 2 mm thickness. Its annealing point is 950°C. The glass has wide applications as envelopes for low pressure mercury vapor lamps.

CODE 7911—This is an ultraviolet transmitting glass with low gas content. It has high electrical resistance and low power loss. It is somewhat harder than Code 7900 or 7910 glasses and can therefore be used at higher temperatures without deformation. The glass was designed for medium pressure mercury vapor lamps. Its ultraviolet transmittance is controlled to at least 85% at 302 millimicrons through one wall.

CODE 7912—This glass has the same overall properties as Code 7910 but is more transparent to wavelengths below 254 millimicrons. Its minimum transmittance at 185 millimicrons is 2% for a thickness of one millimeter. It is available only in tube form and is chiefly used in low pressure mercury arc, germicidal, and ozone producing lamps.

CODE 7913—This glass has a low gas content. It has no special restrictions on transmission. Because of its excellent heat resistance it is used as containers for sintering, calcining, high temperature fusion, and chemical reaction at elevated temperatures. In tube form, it is used as thermocouple protecting tubes and tips, heat sheath tubing, hot-furnace sampling tubes, etc. There are many more applications for this glass. It is available in tubing, rod, sheet, pressed or blown or fabricated ware.

CODE 7913—OPTICAL GRADE—It is made from optical quality base glass and is available in three optical grades. In Schlieren quality, the maximum gradient of the average index of refraction through the blank, measured perpendicular through the window, is held to a minimum of 5×10^{-6} per inch. The optical grade glasses are used in windows for mapping, for wind tunnel applications, in space capsules, or where high internal quality is required for use at elevated temperatures. Maximum size is 20-inch square or 20-inch diameter. Maximum thickness is ¾ inch ground.

CODE 7914—This glass was originally made in tubing form for jackets in mercury vapor lamps. It has at least 20% transmittance at 254 millimicrons, high electrical resistivity and low power loss.

CODE 7915—This glass is intended for severe service of many thousands of hours duration in high pressure mercury vapor lamp applications. It will not darken or solarize. It is nearly 98% silica and is controlled to contain less than 0.002% Na_2O and 0.003% water (determined by infrared adsorption data) to minimize devitrification and outgassing in service. The annealing point is about 1060°C. and Code 7915 glass is least likely to deform at high temperatures. It is available in thin wall tubing.

CODE 7916—This glass has the highest resistance to deformation at high temperatures. It is presently being made in small diameter tubing, known as "core tubing", for manufacture of perforated turbine buckets for jet engines by the investment casting process.

CODE 7930—This glass is usually referred to as "porous glass" or "thirsty" glass. Code 7930 is the intermediate form of porous glass obtained in leaching the base glass used in manufacture of the final fired VYCOR Brand glasses. It has an average pore diameter of 40 angstrom units. Its chief commercial application is as moisture getter in electronic components.

CODE 7931—This number is used to designate clear graded seals fabricated from porous glass tubing in the manner described under heading 6—Graded Seals. The seals are useful for sealing 96% silica glasses or fused quartz to PYREX Brand Code 7740 glass. The soft end is colored blue for identification. Graded seals are available in sizes up to 115 mm O.D. These seals are finding increased applications in both industry and laboratory. They are currently also used in the manufacture of more sensitive photomultiplier tubes.

CODE 7950—This is a red-stained reconstructed glass which absorbs most of the visible light from a tungsten filament (2700°K.) but effectively transmits infrared. It is available in tubing, sheet, blown and pressed ware. In tubing form it is finding increasingly wide application as an envelope for radiant heaters.

CODE 1950—This glass is similar to Code 7915 glass with even more stringent specifications. Like Code 7915, it was also designed for high pressure mercury vapor lamps.

REFERENCES

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MECHANICAL REQUIREMENTS FOR SOLDER GLASS SEALS ON GLASS

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INTRODUCTION

Solder glasses fall into three general types:

1. Vitreous solder glass
2. Devitrifying solder glass
3. Devitrifying-Conductive solder glass

The vitreous type solder glass has a low softening point which, when applied to glasses of higher softening points, makes a seal in a similar way to sealing metals with solder. This sealing is usually done below the annealing point, or just slightly above that of the component parts. The criteria is that the component parts do not deform. This type of solder glass maintains, in the final seal, the same softening point as in its original state so that when parts are reprocessed at the softening point temperature, the glass can readily move or be taken apart. It is also possible to seal glasses to metal parts where co-efficient of expansion properties are similar.

The devitrifying solder glass is quite different in its properties. It is in the vitreous state when applied but after proper thermal cycling it devitrifies or crystallizes; thus, when processed again at its original softening point it no longer softens and can be subjected to temperatures above its original softening point without worries of movement or separation of component parts. This property makes it more desirable than the vitreous type of solder glass where an article must be processed more than once.

The conductive type of solder glass is very similar in properties to the devitrifying type and is of most recent development. The conductive solder glass is proposed for use for both a seal and a low resistance electrical path if needed between the component parts.

VITREOUS SOLDER GLASS APPLICATION

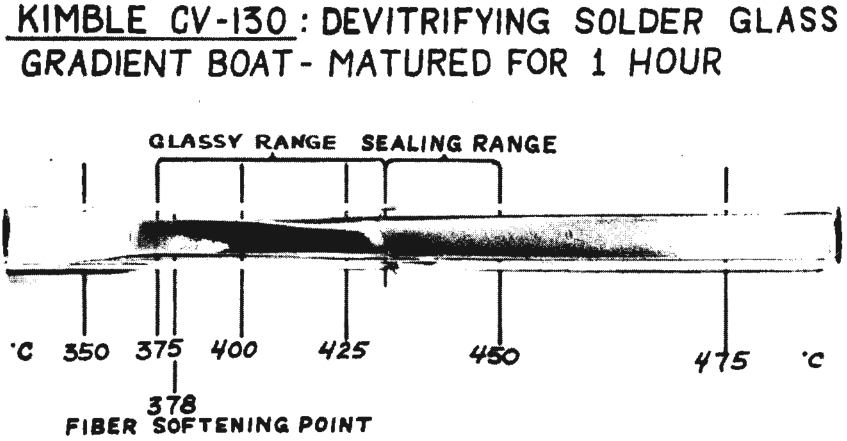
Vitreous solder glasses are easier to process than the devitrifying type because shorter thermal cycles can be used to effect the seal. All that is necessary is to reach the fusion temperatures at a gradient which does not cause heatup breakage, fuse, and cool so that temporary stress does not cause breakage. They are used, in many instances, where it is required to readily separate and reseal the component parts. Normally, the vitreous type of solder glass is lower in strength than the devitrifying type but can be used successfully in many small items.

There are two general methods of application. The first is called "cold application" and is accomplished by taking a finely ground powder and mixing with a vehicle consisting of 1½%Nitrocellulose in Amyl Acetate. This vehicle readily decomposes below the softening point of the solder glass so it does not cause contaminated or seedy seals. The sealing edge must be thoroughly cleaned with alcohol or acetone just prior to solder glass application. Contamination can cause failure from the standpoint of thermal shock and electrical breakdown. The article can be dipped in a rather thin paste or can be applied by using a thick paste which is introduced into a tooth paste or nasal ointment tube and then extruding the desired amount on the sealing edge. Another piece of equipment that can be used is Model #C600 Almite gun which has an orifice made by attaching a piece of ⅛″ I.D. copper tubing. In all cases, excellent green strength is obtained through the use of the Nitrocellulose Amyl Acetate vehicle. In some seals, such as butted pieces of tubing and TV bulbs, the excess solder glass can be removed with a knife or spatula, after drying, without disrupting the sealing edge.

The second method of applying vitreous solder glass is called to "hot dip" method. Here the solder glass is heated in a platinum container far above its softening point, to a point where the solder glass has viscosity close to that of water. The component glass parts or metal parts are usually preheated close to the annealing point of the glass before dipping. The part is dipped into the hot solder glass for 10 - 15 seconds, removed, and held in position for 5 seconds to setup the solder glass. It is then placed back into an oven to anneal. By this method there is a solution of the parent glass by the solder glass and a better seal is obtained. After annealing, the parts can be sealed at a later date by processing at a temperature approximately 75°F. above the fiber softening point of the solder glass. Satisfactory seals can be made by having just one of the component parts pretreated but it has been found that better seals can be obtained by coating both edges prior to sealing. Generally, seals made by the "hot dip" method show a higher seal strength than that of the "cold paste" application.

DEVITRIFYING SOLDER GLASS APPLICATION

The general accepted method of application is to use a finely ground solder glass in paste form and making either a "cold dip" or use of the same devices as the tooth paste tube or mechanical applicator as described under the vitreous solder glass section. The solder glass is usually mixed with a vehicle composed of Amyl Acetate and Nitrocellulose. The maturing temperature cycle is longer for the devitrifying type of solder glass than for the vitreous type. With the devitrifying type there is a range of temperatures where the best seal is made. For example, Figure 1 shows a gradient test boat where a solder glass, in ground



KIMBLE CV-130: DEVITRIFYING SOLDER GLASS
GRADIENT BOAT - MATURED FOR 1 HOUR

Figure 1

form, was poured into a boat and then placed in a gradient furnace for one hour. In the case of this solder glass the glassy range is from 375°C. to 430°C. It has been found with the devitrifying type of solder glass, the longer the glassy range, the more flow, wetting, or filleting will be accomplished in the seal. The actual seal is made between 430°C. to 450°C. for a period of one hour. This example is Kimble CV-130 solder glass for sealing glass and metal with a thermal expansion of (0 - 300°C. from 96 to 104 x 10^{-7}) per degree Centigrade. With this cycle time and temperatures the strongest seal is obtained. Seals can be made at higher temperatures but strength decreases considerably.

KIMBLE CV-101: DEVITRIFYING SOLDER GLASS
GRADIENT BOAT - MATURED FOR 1 HOUR

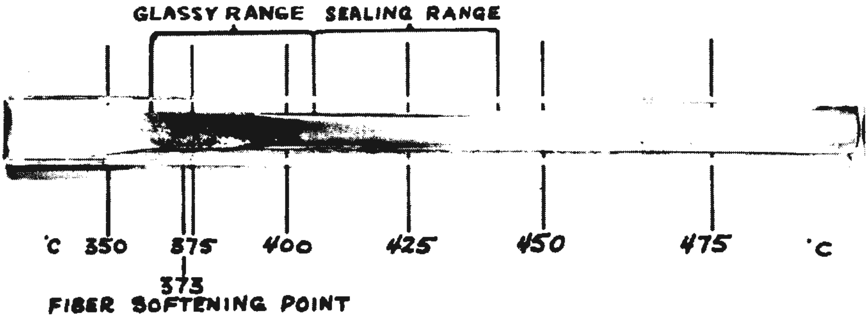


Figure 2

Figure 2 shows another solder glass which can be used for sealing glass and metal from (0 - 300°C. from 80 to 90 x 10^{-7}) per degree Centigrade. Here the glassy range is from 365°C. to 405°C. and the sealing range is 405°C. to 440°C. for one hour.

CONDUCTIVE DEVITRIFYING SOLDER GLASS

Conductive type solder glass is recommended for use as a seal for a low resistivity electrical path. This material can be applied and sealed in the same method as a regular devitrifying type of solder glass. Figure 3 shows a gradient test boat for this type material. Here the glassy range is from 340°C. to 390°C.; this material does not flow and fillet as readily to give the comparable strength of the seals. With this solder glass a seal is best made at a temperature of 425°C. plus or minus 5°C. for one hour. At a lower temperature, the seals would not be vacuum tight while at the higher temperatures, loss of conductivity is experienced. Reheating of the seals can be accomplished if the temperatures do not exceed the recommended maximum of 450°C.

SEAL STRUCTURE

Solder glass is well adapted to make many types of seals. Figure 4 shows a butt type seal. Figure 4A is a very undesirable and weak type due to the reentrant angle and non-filleting of the solder glass. It is brought about by sealing

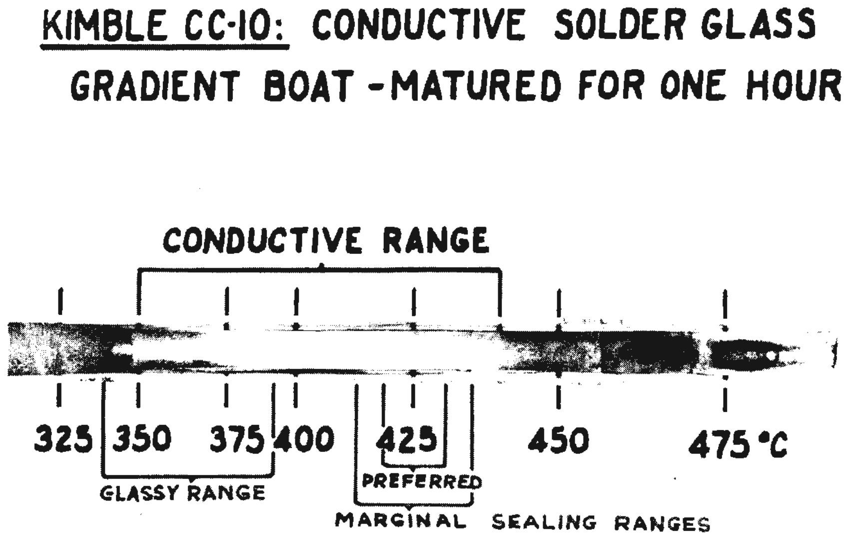


Figure 3

the solder glass on the seal edge only and not having enough flow in the solder glass. Figure 4B is a better and stronger seal but still has a weakness caused by the re-entrant angle. This type is usually caused by having the solder glass on the sealing edge only and forcing the solder glass out, by pressure, during the sealing operation. The solder glass has very little flow. Figure 4C is the best type of seal, well filleted with no re-entrant angle. To obtain this type of seal one must either have an excellent flowing solder glass or coat the sealing edges with a paste prior to sealing. Figure 4D has been coated with a solder glass that had poor filleting characteristics. Figure 4E shows the strongest type of seal, where the one seal edge is wider than the other. With a good flowing solder glass, sufficient paste can be applied to the thicker sealing edge and the thinner edge simply placed on top of the solder glass; through gravity or pressure a strong seal can be effected.

Figure 5 shows various types of seals obtained with a flat plate and a ring section. Figure 5A is undesirable because of re-entrant angle caused by solder glass with no flow and no pressure to produce flow. Figure 5B is a solder glass with little flow but has pressure applied in the sealing cycle. This type of seal can be utilized but is not the best. Figure 5C illustrates the most desirable type of seal where the solder glass has flowed and filleted well.

Figure 6 shows the evolution in designing a large article which contains a vacuum. The strength of these seals was evaluated by pulling a vacuum on the article, cooling it to a uniform, desired temperature with water, then flooding it with hot water at progressive specific temperature differentials to provide thermal shock to the inside surface until failure occurred. Figure 6A shows a seal which has the same width sealing edges and a fairly well filleted solder glass. This type seal is weaker than those in Figure 6B, 6C, and 6D. Figure 6B shows a wider sealing edge with a narrower section being contained in between which produces a strong type seal. Figure 6C and 6D show variations of this wider sealing edge on one side and also shows the increased strength obtained by design. The table incorporated in Figure 6 shows the development data and the increased thermal durability by various seal contour combinations.

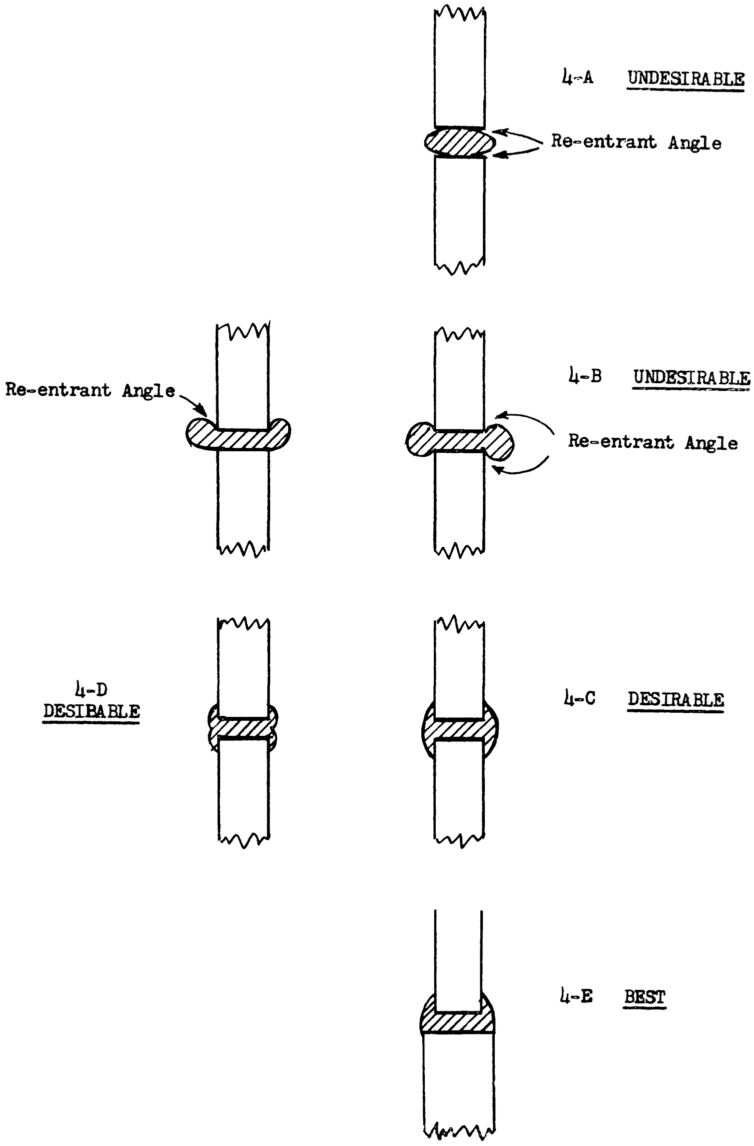


Figure 4
"Butt Seal" Solder Glass Sealed Sections

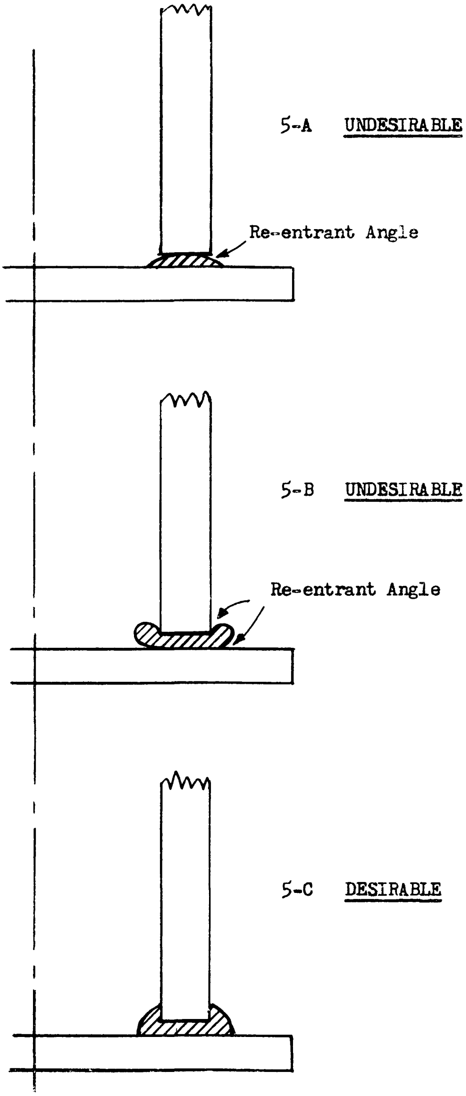
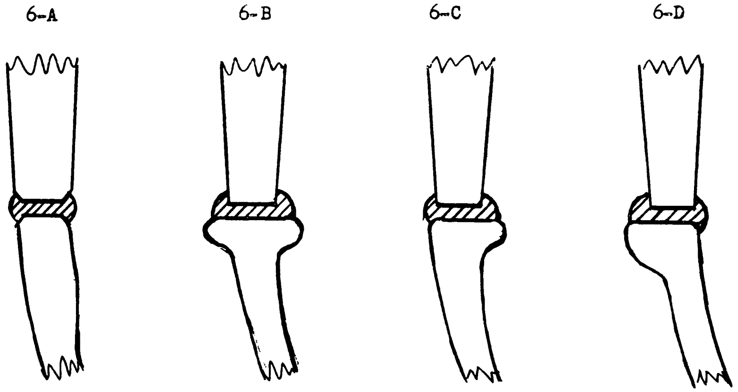


Figure 5
Glass/Metal Ring or Plate Seals



Failure in Inside-Evacuated Thermal Shock Tests

Broke at Temp Diff. °F	6-A	6-B	6-C	6-D	Broke at Temp Diff. °F
80	X				80
90	X				90
100	X				100
110			X		110
120			X	X	120
130			X	X	130
140	X				140
150					150
Passed					Passed
150			X X	X X X	150
160		X X X X			160

Figure 6
Designs Evolving from Tests on Large Evacuated Articles

WHAT THE SCIENTIST EXPECTS FROM A GLASSBLOWER TODAY

DR. JOHN TURKEVICH
Professor of Chemistry, Princeton University
Princeton, New Jersey

Mr. Chairman, Ladies and Gentlemen:

I am highly embarrassed after this long introduction. This is something I am afraid of but have to live with as the years go by. I am very happy to be here. I made a very special point to do so, since my time is a bit tight. I'm leaving next Saturday for Moscow and Warsaw and I'm going to be in Moscow at the American Science Laboratory at the Embassy advising the ambassador of scientific things in the Soviet Union in general and keeping my eyes open to see what our friends are doing over there.

I would like to point out to you today where I think you fit in and we scientists fit in in the general picture in the modern day. I don't think enough people outside the scientific profession appreciate the importance of science in modern day. It just so happens that in the last fifty, sixty years and quite possibly for the next sixty years and after that we won't care too much, science has topped all, science dominates the picture, science and technology, and what the scientist does for the development of a better way of living, changing the world, is going to depend, as it did depend in the past, on what you people do. The art of glass blowing, the handling of glass, and your art extended to other materials is absolutely essential to scientific development. And the little things which you do in perfecting materials, handling more complicated systems, translating crazy ideas, and some of these ideas that scientists are praising, into something practical that he can do, is something that the general public does not appreciate. My colleagues in the scientific field are highly dependent and very thankful. The little jobs which were done in the past for us in carrying out our scientific work may be forgotten by you but many of us remember that it was the glass blower with whom we worked who made the job possible by doing something that was first seemingly impossible, or advising the scientist; Look can't you change it this way, can't you simplify it, maybe you can get the same result. But from this point of view, the scientific glass blower, as dominant as anybody in scientific development, led to atomic energy and to space work and I don't think there is any question that it is going to continue so we are going to make greater demands of you. We might for a minute say there are other materials coming in that are going to displace glass, materials that can be carried on using the art that has a great tradition, the art of glass blowing. I won't be worried about that. It still will require the skill, the brains and the adaptation to practical work that the glass blower contributes in the scientific enterprise. And I also can assure you while there are other materials; plastics, metals, possibly some ceramics are coming into use, the demands are so great for people of your skill, that not only you but many many more will be required to handle the demands of science in their work in trying to figure out new ways of handling matter and learning more about nature. As you've heard, I have been in the teaching profession for a long time. One of the things I felt very strongly about, my friend Lee Harris, who worked at Princton Laboratory doing glass blowing, will recall, tried to get as many undergraduates who were taking elementary chemistry, 300, the Chairman talked about, to get some appreciation of glass blowing. And while these fellows were being so high fillutin, so learned, that they didn't know that glass breaks. They would be the best testing machines. They can drop them faster and better than any machine can drop them. One of the things we have to do is teach them that there is a limit to anything; there is a limit to the strength of glass. If you start messing around too much with it you not only break it but you hurt yourself. I was introduced in the past for almost 15 years to elementary glass blowing at the freshman level in our chemistry course. That's just bending glass and joining glass together. There's absolutely no danger that we are turning out competitiveness to you, but these fellows don't do much beyond that. But they do appreciate some of the difficulties involved in handling glass. So we can say, we can urge, and I think one of the activities in your Society should be to inculcate just a little bit of glass blowing to all the elementary science college courses in their laboratory, so they can appreciate your work better, because they will conceive very rapidly your excellence and decry the inaptitude of their fingers. One of the things you learn is that you never take a specimen that the student hands you because you will burn yourself very rapidly. The other place in science where glass blowing come in in my particular work is the graduate student; the man working in chemistry, physics, biology, with glass, the vacuum system boys. When I started off in the early thirties, part of the thesis was essentially glass blowing because we had to build an apparatus out of pieces of glass. In those days we still had to work with soft glass and some of us had the unfortunate situation in inheriting somebody elses old soft glass apparatus, and I and my colleagues of that era can remember how starting off with a little break on a rather big rack, started fixing it up, and by the end of the day having nothing. As you fixed it up, more and more would break and the whole thing would go. But the problem was that it didn't break in one day, you see, because if it broke in one day, then you'd start from scratch and get somewhere. You were always kidding yourself that if I patch this thing up, the rest is going to hold up. Well the rest went the following week. So this is how a whole year went out. At that time in my field of physical chemistry, glass blowing was about as important an art to carry out research as weighing or mixing chemicals together. And all of us had to blow glass. It was only in those days, we were even proud; we wouldn't go to a man like Lee Harris and ask him to do a job unless we broke something like a diffusion pump. These days are gone. I find among the graduate students very few who can build a vacuum system. And it's just as well. After all, due to the expansion of science, due to the expansion of your own organization and group, there was a competent glass blower, certainly at least one, in each major research organization. And that being the case, why should people getting a doctorate degree spend their time hacking and building vacuum systems and other equipment that seems to have that pernicious habit of breaking just at the time when you are doing a most important experiment. That's not their job. The job of the professional scientific glass blower is to build the system for him. And we've got to get more and more people to appreciate the fact that there has to be a very close interplay between the ideas of the scientist, and particularly the young scientist, and the people practicing your art because you can make or break a given scientific investigation. I'll never forget one young fellow, graduate student, who seemed like he knew it all and made fun of our glass blower, Mr. Wilson, long passed away, and gave him a hard time, gave him a rough time. Old Wilson got back at him. This fellow was building a vacuum system, and he gave him all second grade stop cocks. That ruined him for a whole year you see. It was very, very difficult to find out just what was happening. So this story I tell to my friends.

But in the interplay of science that we have with art, technology, the contribution to a scientific piece of work of a glass blower, mechanic, electronics man is just as significant as some of the ideas that one has because the ideas in physical science don't go much beyond their translation into the materials that you have. As one looks through the quick scientific development that is taking place right now, actually changing the world in the last fifty-sixty years, the contribution of the scientific glass blower is dominant, as I said before; I would say as important a development as any that laid the basis for the present scientific age is the development of a glass apparatus that can stand a vacuum. The old vacuum pump, the Toepler pump, used by Mr. Edison over here in New Jersey, was a glass blower's job, done well. It was by being able to control the vacuum that all the electronic gadgets started out with, a discharge tube, photo electric tube, the X-ray tube; from the X-ray tube and work with X-rays, radioactivity was discovered, the Geiger counter tube. All the various components that make modern science what it is are essentially glass blowing jobs. And you can go down to even modern days, lovely and interesting developments that intrigued us in ultra high vacuum, falls into the properties of glass.

For you gentlemen have a very very honorable tradition, a great history, a great record of cooperation that the scientific profession is going to have a glorious future. But this future is going to make demands both on you and on ourselves. I taught a course in chemical techniques and manipulation for graduate students, future scientists, among other things, telling them about the properties of glass and what they can expect in a reasonable way from a glass blower. We'll have to revise that. I think that something that we will have to consider in this organization is having some kind of a handbook, and getting someone to tell the kinds of seals and techniques that are available so that he may know some of the recent developments that you and your art have developed. And we will have to know more and more of what you can do. Because by asking you to do what seems to you at first to be impossible, we are going to develop your skill by that challenge and at the same time solve problems which, without you, we never could handle.

A BAKEABLE DIFFUSION PUMP ASSEMBLY FOR ULTRA HIGH VACUUM

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INTRODUCTION

The achievement of ultra-high vacuua requires extensive bakeout of all parts of the vacuum system including, if possible, the high vacuum jet and condenser assembly of a diffusion pump used as part of such a system. Such a technique has been described in the literature[1] as being successful in attaining pressures in the 10^{-12}mm Hg range. However, this has been accomplished at the expense of employing an auxiliary diffusion pump to maintain the necessary high vacuum while the pump being baked is thereby rendered inoperative. This situation results from the fact that conventional diffusion pump designs do not lend themselves to operation as a pump during bakeout. Even if only the high vacuum jet is being baked, there would be excessive backstreaming of uncondensed mercury discharged in the heated jet assembly. A two-stage pump has been designed and tested in which a cut-off is provided between the first and second stages so that the high vacuum jet (and associated structure) may be rendered inoperative and baked out while the first stage continues to function and maintains the required high vacuum in the system.

DESCRIPTION

The two jet assemblies with the cut-off between them are shown in Figure 1. Figure 2 is a drawing of the cut-off in the closed condition. The tube which conducts mercury vapor from the lower jet of the pump to the upper jet is intercepted by this assembly.

The glass walled heater bulb is so shaped that its lower end forms a lip surrounding the re-entrant edge of the tube which provides the mercury flow path. The heater bulb contains a ¼″ diameter coil consisting of 10 turns of .010″ tungsten and is filled with a few mm Hg pressure of Argon. The gas fill is for the purpose of better conducting the heat from the heater to the walls of the bulb. The connections from the tungsten coil are brought out through glass to metal seals in the wall of the pump body, a gap between two parts of the divided pump water jacket being provided for this purpose. The divided pump jacket also permits draining the upper section separately during upper pump bakeout.

A small water jacket surrounds the cut-off as shown. The water connections to it penetrate the wall of the pump body through ring seals, again in the gap between the two parts of the water jacket.

CONSTRUCTION

The heater bulb #1, Figure 1 is made of 7052 glass with .040 kovar leads which act as support for the bulb as well as supplying power to the heater. The bulb is made in such a way that the lower lip extends down about $\frac{1}{16}$″ over the re-entrant edge of the mercury flow tube #4.

The cut-off water jacket extends from the top of the heater bulb down around the bulb to the mercury flow tube. The water lines for the water jacket are bent

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[1] A Venema and M. Bandringa, *Phillips Technical Review,* Vol. 20, pp. 145-157 (1958).

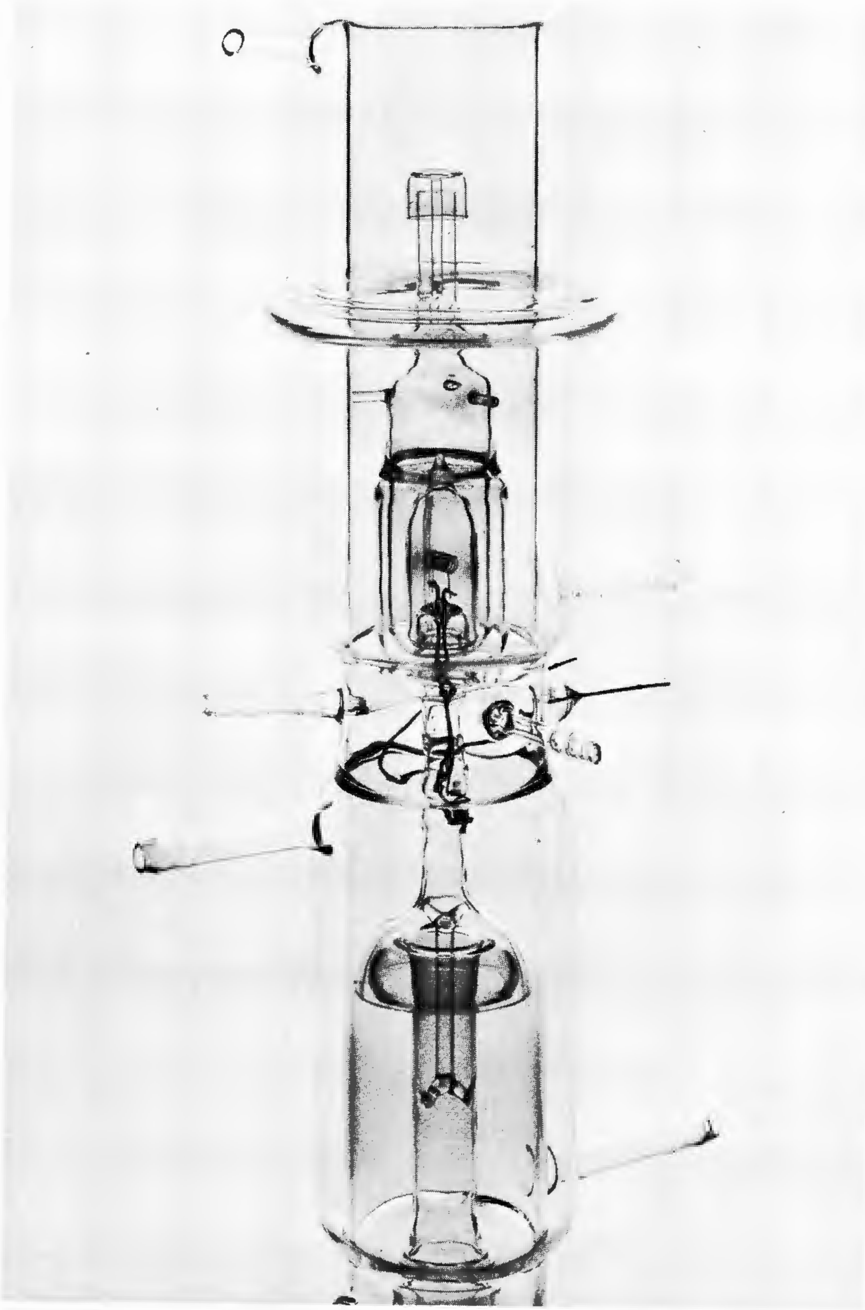

Figure I
Interstage cut-off and jet assembly

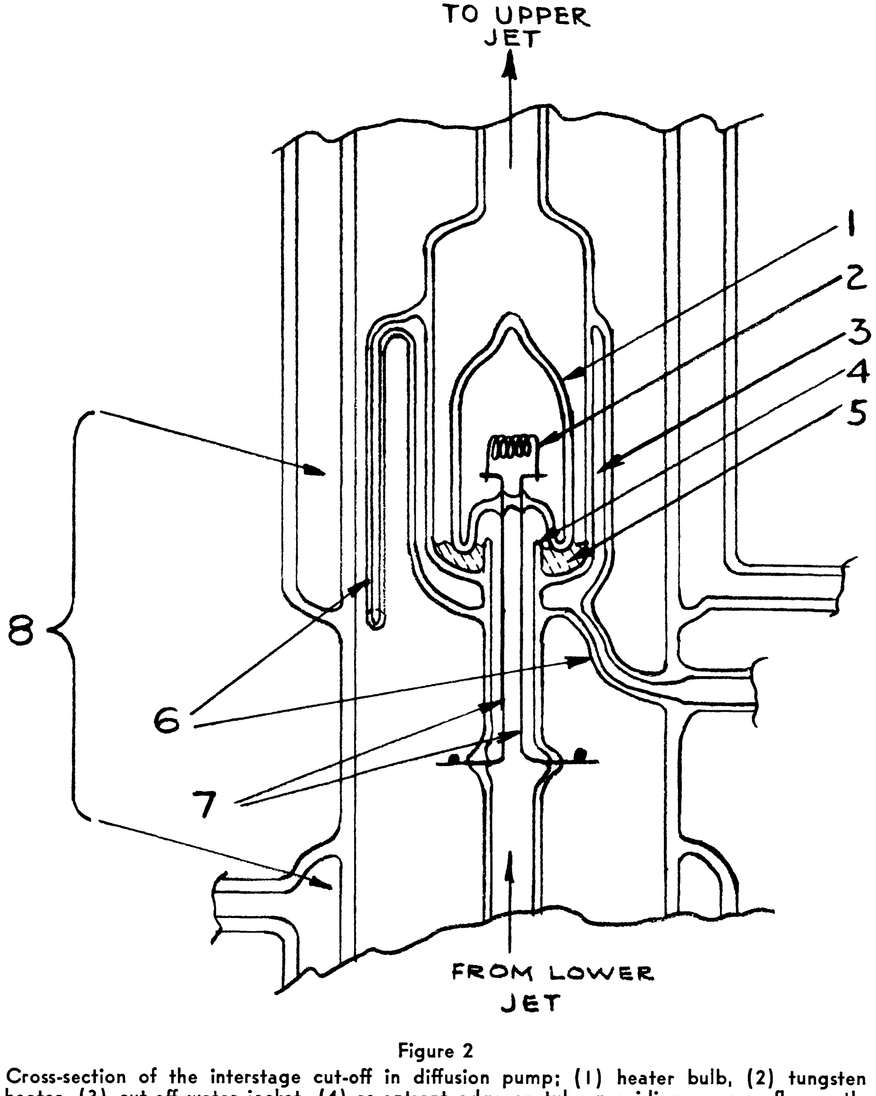

Figure 2
Cross-section of the interstage cut-off in diffusion pump; (1) heater bulb, (2) tungsten heater, (3) cut-off water jacket, (4) re-entrant edge on tube providing mercury flow path, (5) mercury puddle, (6) cut-off water jacket tubulations, (7) heater leads, (8) divided water jacket or diffusion pump.

down and out to the inside wall of the pump at the point where the outer water jackets are divided.

The kovar heater leads extend down through the mercury flow tube to a section of 7052 glass provided for the kovar to glass seals. The flow tube was cut at the center of the 7052 section and the heater bulb was inserted into the water jacket with asbestos spacers for alignment. The beaded leads extend beyond the cut end to allow a 90° bend to bring the heater leads through the wall of the mercury flow tube; the two parts of the flow tube, together with the beaded leads are then sealed in one operation.

Flexible leads were spot welded to these leads making it possible to pull them through holes provided for them in the outer wall of the pump.

Both jet assemblies and the mercury cut-off were sealed to the double flare assembly which in turn is inserted into the pump making sure that the water lines and heater leads are in position to be sealed through the single wall divided area between the outer water jackets. Short tubulations terminating with 7052 glass were used to bring the kovar leads through the outer wall.

Some difficulty was experienced in bringing the small water lines through the outer wall due to the difference in wall thickness of the two parts, however, this could be avoided by sealing a short length of larger tubing to the end of the small tubes prior to inserting the cut-off into the pump, and, therefore, giving a closer match between the inner water lines and the larger outer tubulations.

OPERATION

The closed condition illustrated is achieved by circulating water through the small water jacket which surrounds the cut-off while the tungsten heater is without power. Under these conditions, mercury vapor from the lower part of the pump condenses in the trapping region formed by the lip at the bottom of the heater bulb and the re-entrant edge of the tube which provides the mercury flow path. A puddle of mercury is thus formed which is maintained at a low temperature by the water jacket and effectively prevents mercury vapor from traveling to the upper jet.

By draining water from the upper part of the pump water jacket and applying heat to the region above the cut-off assembly, the upper jet assembly may thus be baked so as to outgas this part of the pump as dictated by good ultra high vacuum practice.

The open condition of the cut-off is achieved by draining the cut-off water jacket and passing current through the tungsten heater, raising its temperature to approximately 800°C. In this way sufficient additional heat is supplied to the mercury puddle to evaporate it, opening the cut-off. After this occurs, sufficient heat must still be supplied to the mercury stream incident upon the trapping region so that the mercury puddle does not re-form. Therefore, the 800°C. temperature of the tungsten heater is maintained throughout the period of normal operation of the pump.

PERFORMANCE

A complete pump and cold trap assembly was constructed incorporating the inter-stage cut-off in order to test its operation. The lower stage jet and boiler assembly were modeled after that of Venema and Bandringa.[1] A Harwell Metallurgh Department design cold trap was used because it is particularly suitable for an in-line arrangement of the pump and trap thus facilitating complete system bakeout. Figure 3 is a photograph of this structure. A CVC type GIC-013 ionization gauge together with a glass capillary leak were added so that the pumping speed could be measured. The capillary leak was previously calibrated

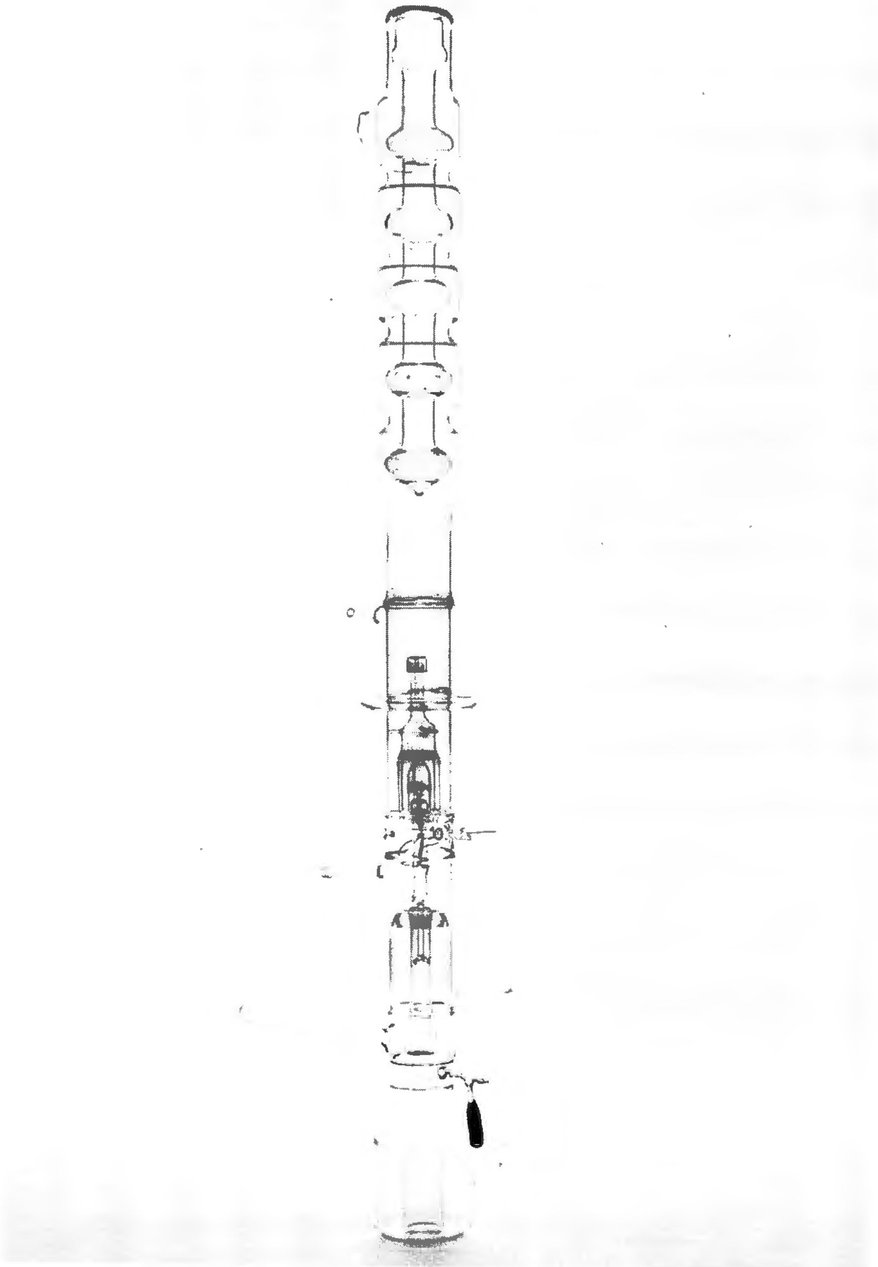

Figure 3
Pump and cold trap assembly

by observing the rate of pressure rise in a known volume to which it was attached. Its value under the conditions used (high vacuum in system with leak exposed to 157 mm pressure of air) was 10^{-4} cc/sec.

The pump was placed in operation with water circulating in the cut-off jacket and no power to the cut-off heater. The cut-off trapping region became filled with mercury after about 30 minutes and remained so as long as this operating condition was maintained. The pumping speed of the lower stage only, the upper jet being completely inactive, was 4.2 liters/sec.

The cut-off water jacket was drained and the internal heater turned on at a power of 25 watts. After 40 minutes the cut-off cleared itself of mercury and the upper jet became fully operative. The measured pumping speed with both stages functioning was 10 liters/ second. The performance of the cut-off in this open condition was tested with various heater powers, 14 watts being found marginally sufficient to maintain a free passage for mercury vapor and no noticeable improvement in performance being observed above 25 watts.

The pump was operated over a period of several weeks with the interstage cut-off in both closed and open condition for extended periods during which it functioned satisfactorily at all times. Cold trap and upper jet assembly bakeouts were carried out on several occasions after which the pressure achieved appeared to be limited by the extent to which the ionization gauge could be outgassed, a value of 7×10^{-9}mm Hg being the lowest observed.

IN ATTENDANCE

The following are on record as having attended the Sixth Symposium on the Art of Glassblowing held at the Hotel New Yorker, New York City, on May 24, 25, and 26, 1961. As a fully registered participant, these persons are entitled to a copy of the "Proceedings".

In addition to the names listed here-in, 130 persons registered by day card, and 135 to attend the exhibit only.

Abrahammer, Ralph	Fisher Scientific Co., 633 Greenwich St., N. Y., N. Y.
Airey, Andrew	Smith, Kline & French Labs., 1530 Spring Garden St., Phila., Pa.
Alexander, J. Allen	The Atlantic Refining Co., Res. & Dev. Dept., 2700 W. Passyunk Ave., Phila. 45, Pa.
Altosaar, H.	Dominion Tar & Chemicals Co., Cornwall, Ont., Canada
Ammons, A. R.	Friedrich & Dimmock, Inc., Millville, N. J.
Anderson, Elmer F.	Ryan, Velluto & Anderson, Inc., 103 First St., Cambridge, Mass.
Anderson, Frederick F.	Ciba Pharmaceutical Products, Inc., Summit, N. J.
Arns, Theodore	Brookhaven National Lab., Upton, N. Y.

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